

UNIVERSITY OF WOLLONGONG

DOCTORAL THESIS

---

**Thesis Title**

---

*Author:*  
Jesse GREENSLADE

*Supervisor:*  
Dr. Jenny FISHER

*A thesis submitted in fulfillment of the requirements  
for the degree of Doctor of Philosophy  
in the*

Centre of Atmospheric Chemistry  
Chemistry Department

February 20, 2018



## Declaration of Authorship

I, Jesse GREENSLADE, declare that this thesis titled, “Thesis Title” and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

---

Date:

---



*"Thanks to my solid academic training, today I can write hundreds of words on virtually any topic without possessing a shred of information, which is how I got a good job in journalism."*

Dave Barry



# Contents

<b>Declaration of Authorship</b>	<b>iii</b>
<b>1 Introduction and Literature Review</b>	<b>1</b>
1.1 The atmosphere	1
1.1.1 Structure	1
1.1.2 Chemistry	2
Hydroxyl radicals	2
NO <sub>x</sub>	3
1.2 Ozone	3
1.2.1 Stratosphere to troposphere transport	5
1.2.2 Chemical production	6
1.3 VOCs	8
1.3.1 Isoprene	9
1.3.2 Emissions	10
1.3.3 The isoprene cascade	10
Oxidation	11
Ozonolysis	13
Oxidation by NO <sub>3</sub>	13
1.3.4 Radiative Forcing	13
1.4 HCHO	14
1.4.1 Sources and sinks	14
1.4.2 Measurement techniques	18
Satellite measurements	19
1.5 Atmospheric Chemistry Modelling	19
1.5.1 Box models	22
1.5.2 Emissions	22
1.5.3 Uncertainties?	23
Emissions Inventories	23
Resolution	24
Chemistry mechanisms	25
Clouds	25
Soil Moisture	25
1.6 Australia and the southern hemisphere	26
1.6.1 Ozone	27
1.6.2 VOCs	27
1.6.3 Measurements	28
1.7 Aims	29





# List of Figures

1.1	Pressure (red) logarithmically decreasing, shown with percentage of atmosphere below at several points. Temperature (green) changes throughout the atmosphere. Figure edited from <a href="https://climate.ncsu.edu/edu/Structure">https://climate.ncsu.edu/edu/Structure</a> . . . . .	2
1.2	Tropospheric ozone processes, Figure 1 in Young et al., 2017. DOI: <a href="https://doi.org/10.1525/elementa.265.f1">https://doi.org/10.1525/elementa.265.f1</a> . . . . .	5
1.3	Ozone production figure copied from Mazzuca et al., 2016. . . . .	7
1.4	The overall radiative forcings and uncertainties of several atmospheric constituents This is an image taken from Forster et al., 2007, found at <a href="https://www.ipcc.ch/publications_and_data/ar4/wg1/en/faq-2-1.html">https://www.ipcc.ch/publications_and_data/ar4/wg1/en/faq-2-1.html</a> . . . . .	15
1.5	The overall radiative forcings and uncertainties of several atmospheric constituents This is an image taken from <i>IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change</i> , chapter 8. . . . .	16
1.6	HCHO spectrum, with a typical band of wavelengths used for DOAS path measurements. This is a portion of an image from Davenport et al., 2015. . . . .	18
1.7	An example spectrum showing interferences used for species concentration measurements by GOME-2. Image by EUMETSAT and ESA (EUMETSAT, 2015). . . . .	20
1.8	Standard box model parameters, image taken from Jacob, 1999. . . . .	22
1.9	Part of a figure from Guenther et al., 2006 showing global isoprene emission factors. . . . .	27



## List of Tables



## Chapter 1

# Introduction and Literature Review

### 1.1 The atmosphere

The atmosphere is made up of various gases held to the earth's surface by gravity. These gases undergo transport on all scales, from barbecue smoke being blown into your face to smoke plumes from forest fires travelling across the world and depositing in the antarctic snow. They take part in various chemical reactions along the way, largely driven by solar input and interactions with each other. Various chemicals are lofted into the atmosphere by soil, trees, factories, cars, seas and oceans, you name it. They are also deposited back to the surface both directly and in rain drops.

Mostly the atmosphere is made up of nitrogen ( $\text{N}_2$ :  $\sim 78\%$ ), oxygen ( $\text{O}_2$ :  $\sim 21\%$ ), and argon ( $\text{Ar}$ :  $\sim 1\%$ ). Water ( $\text{H}_2\text{O}$ ) ranges from 0.001 to 1% depending on evaporation and precipitation. Beyond these major constituents the atmosphere has a vast number of *trace gases*, including carbon dioxide ( $\text{CO}_2$ :  $\sim 0.4\%$ ), Ozone ( $\text{O}_3$ : .000001 to 0.001%), and methane ( $\text{CH}_4$ :  $\sim 0.4\%$ ) Brasseur and Jacob, 2017, Ch. 2. Trace gases in the atmosphere can have a large impact on living conditions. They react in complex ways with other elements (anthropogenic and natural), affecting various ecosystems upon which life depends.

Most of the atmosphere ( $\sim 85\%$ ) is within 10 km of the earth's surface. This is due to air pressure, which decreases logarithmically with altitude. Imagine you are lying at the bottom of the ocean, except that ocean is made up of air. The pressure we are subjected to is from the weight of all the air above us.

#### 1.1.1 Structure

The atmosphere extends above us to the edges of space. This is split into various layers, defined by the *lapse rate*: the decrease in temperature as we ascend. Figure 1.1 shows the pressure and temperature profiles as we head upwards through the atmosphere. First we have the troposphere, which extends to roughly 10 km and is characterised by increasing positive lapse rate (or decreasing temperature with altitude). At the top of the troposphere (the tropopause) the temperature stops decreasing, and then the stratosphere is defined by a negative lapse rate. This is due to UV light being absorbed by ozone, and leads to a very vertically stable environment.

In addition to these atmospheric layers, it is helpful to split the troposphere further: into a *boundary layer*, and the *free troposphere*. The *boundary layer* is the lowest layer and involves increased atmospheric mixing due to ground heating and friction effects. It generally extends anywhere from 200 - 1000 m, above which the ground affects have

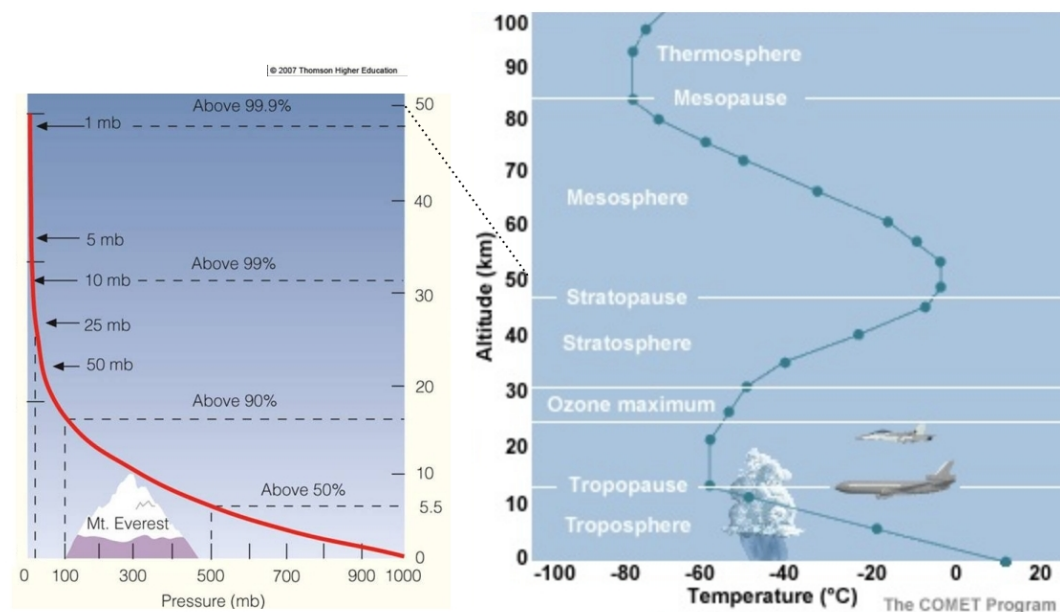


FIGURE 1.1: Pressure (red) logarithmically decreasing, shown with percentage of atmosphere below at several points. Temperature (green) changes throughout the atmosphere. Figure edited from <https://climate.ncsu.edu/edu/Structure>.

less direct impacts. The *free troposphere* is the remainder of the troposphere and is more affected by transport, both horizontally and from the stratosphere.

## 1.1.2 Chemistry

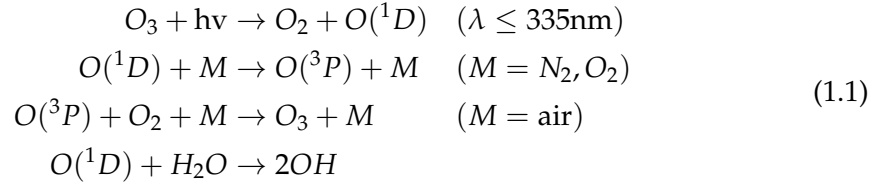
### Hydroxyl radicals

The OH radical drives many processes in the atmosphere, especially during the day when photolysis of ozone drives OH concentrations (Atkinson, 2000). OH is a key species which reacts with nearly all the organic compounds in the troposphere. The exceptions are chlorofluorocarbons (CFCs), and Halons not containing H atoms (Atkinson, 2000). OH and HO<sub>2</sub> concentrations largely determine the oxidative capacity of the atmosphere. Oxidation and photolysis (splitting by photons) are the two main processes whereby compounds are broken down in the atmosphere. Over land, isoprene (C<sub>5</sub>H<sub>8</sub>) and monoterpenes (C<sub>10</sub>H<sub>16</sub>) account for 50% and 30% of the OH reactivity respectively (Fuentes et al., 2000).

In the late 90's it was thought that OH radicals are formed exclusively from photolysis of O<sub>3</sub>, HONO, HCHO, and other carbonyls (R<sub>2</sub>C=O) Atkinson, 2000. Isoprene (C<sub>5</sub>H<sub>8</sub>) was thought to be a sink of OH until it was shown by Paulot et al., 2009b that the radicals are recycled. This recycling process is discussed in more detail in section 1.3.3.

Ozone is an important precursor to OH, as excited oxygen atoms (O(<sup>1</sup>D)) are created through its photolysis, which then go on to mix with water and form OH, as

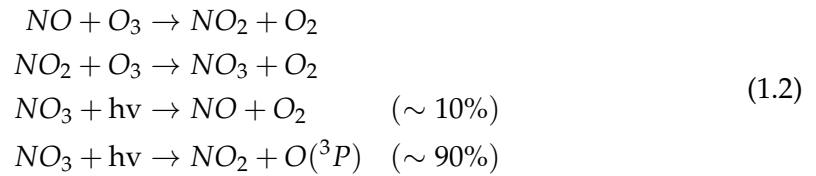
shown in this equation taken from Atkinson, 2000:



This shows how some of the  $O(^1D)$  recycles back to Ozone, while some forms OH. NB: The wavelength was updated to 350 nm in Atkinson and Arey, 2003.

### NO<sub>x</sub>

NO<sub>x</sub> ( $\equiv$  NO<sub>2</sub> and NO) is another important group in the atmosphere due to the various reactions it initiates. Power generation and combustion transport emissions are the main source of NO<sub>x</sub>. If NO and O<sub>3</sub> are both in the atmosphere, the following reactions (Atkinson, 2000) occur:



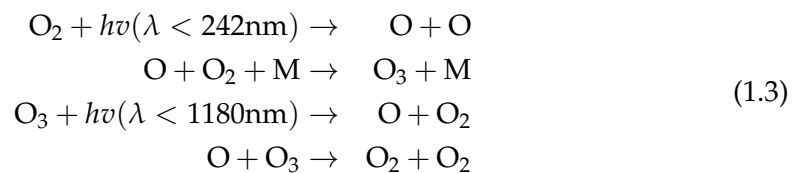
Which generally leads to lower ozone concentrations in cities due to the NO<sub>x</sub> pollution.

Since radicals play such a big role in regulating many chemical reactions in the atmosphere it's important for models to accurately represent them (eg. Travis2014). This is difficult as they are coupled with so many other species and measurements of OH are not readily available on a global scale.

## 1.2 Ozone

Ozone (O<sub>3</sub>) is mostly located in the stratosphere, where it helpfully prevents much of the shorter wave length solar radiation from reaching the earth's surface (ie UV light). In the stratosphere ozone production is generally driven by the Chapman mechanism, as high energy light (with wavelengths  $\lambda < 242$  nm) photolyses the molecular oxygen (O<sub>2</sub>) in the atmosphere (Brasseur and Jacob, 2017, Chapter 3, section 2).

The Chapman mechanism involves several equations which lead to rough equilibrium of O, O<sub>2</sub>, O<sub>3</sub> and pressure, as follows:



Where  $h\nu$  represents radiation and M is an inert molecule (such as  $N_2$ ). The high energy photons ( $\lambda < 242$  nm) are present from the top of the atmosphere but are mostly removed before reaching the troposphere. The lifetime of O against loss by  $O_2$  is less than a second in the troposphere, and produced  $O_3$  quickly returns to O and  $O_2$ , as low energy ( $\lambda < 1180$  nm) light and M are abundant. The gradient of light penetration in addition to the logarithmic decrease in atmospheric pressure (which affects M abundance) drives the vertical profile of ozone into what is called the ozone layer, where we have relative abundance of ozone in the stratosphere. This mechanism requires radiation so only takes place during the daytime, during the night there are different processes driving ozone chemistry.

Ozone in the lower atmosphere is a serious hazard that causes health problems (Hsieh and Liao, 2013), damages agricultural crops worth billions of dollars (Avnery et al., 2013; Yue et al., 2017), and increases the rate of climate warming (Myhre and Shindell, 2013). Around 5 to 20 percent of all air pollution related deaths are due to ozone (Monks et al., 2015), roughly .8 million deaths per year (Lelieveld et al., 2013). In the short term, ozone concentrations of  $\sim 50$ -60 ppbv over eight hours or  $\sim 80$  ppbv over one hour are agreed to constitute a human health hazard (Ayers and Simpson, 2006; Lelieveld et al., 2009). Long term exposure causes problems with crop loss and ecosystem damage (Ashmore, Emberson, and Murray Frank, 2003), and worryingly, concentrations may get worse in the future (Lelieveld et al., 2009; Stevenson et al., 2013). Further tropospheric ozone enhancements are projected to drive reductions in global crop yields equivalent to losses of up to \$USD<sub>2000</sub> 35 billion per year by 2030 (Avnery et al., 2013), along with detrimental health outcomes equivalent to  $\sim$ \$USD<sub>2000</sub>11.8 billion per year by 2050 (Selin et al., 2009). Recently Yue et al., 2017 showed that the net effect of near-surface ozone on is a  $\sim 14\%$  decrease in net primary productivity (NPP) in China. They state that drastic measures could reduce the decrease by  $\sim 70\%$  by 2030.

Since the Montreal Protocol on Substances that Deplete the Ozone Layer was established in August 1987, and ratified in August 1989, several satellites and many measurement stations were set up to monitor ozone in the stratosphere. However, in the southern hemisphere there are relatively few records of ozone (Huang et al., 2017). This affects our ability to accurately determine sources of ozone in the troposphere.

Models of ozone in the atmosphere are used broadly for international assessments of ozone related emissions (Young et al., 2017). Young et al., 2017 summarise current global ozone modelling standards and the metrics and processes used to evaluate these models. They show how models can be used to improve measurements, estimate concentrations in regions not sampled, and allow analysis of other processes which involve ozone (such as radiation).

Generally there are two main drivers of tropospheric ozone concentrations; transport from the stratosphere and production due to emissions of precursors. Globally, most tropospheric ozone is produced by naturally emitted (biogenic) precursors. At small to medium scales, pyrogenic (fire) and anthropogenic (man-made) emissions can be important. Smoke plumes from biomass burning can carry ozone precursors, creating higher ozone concentrations downwind of the plume's source. Emissions of precursors from large cities (such as  $NO_x$  emissions from traffic and power production) can impact ozone concentrations.



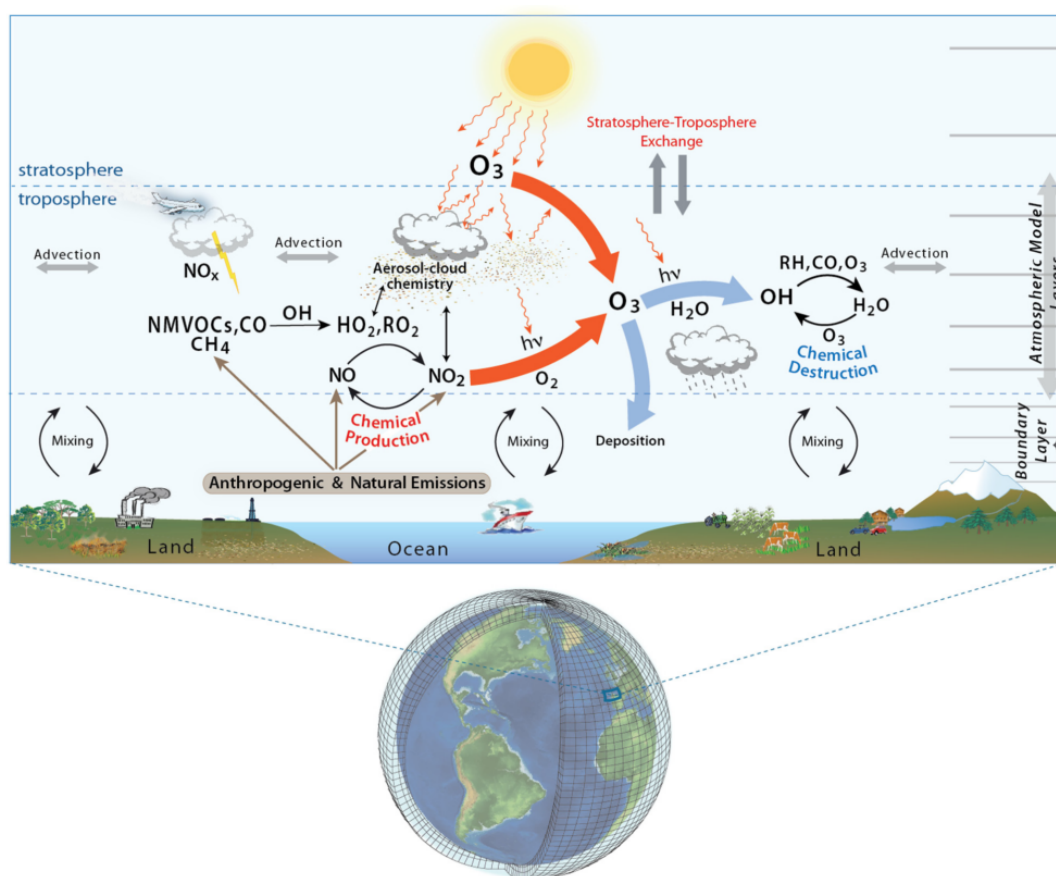


FIGURE 1.2: Tropospheric ozone processes, Figure 1 in Young et al., 2017. DOI: <https://doi.org/10.1525/elementa.265.f1>

A good summary of processes affecting tropospheric ozone, copied from Young et al., 2017, is shown in Figure 1.2. This picture shows the major processes used by global chemistry models when simulating tropospheric ozone. In each gridbox both physical and chemical processes need to be accounted for.

### 1.2.1 Stratosphere to troposphere transport

Historically (in the late 1990's), ozone transported down from the stratosphere was thought to contribute 10-40 ppb to tropospheric ozone levels, matching tropospheric production (Atkinson, 2000; Stohl et al., 2003). This number was revised down over the years as measurement and modelling campaigns improved our understanding of global scale transport, mixing, and chemistry (Monks et al., 2015). Recently Kuang et al., 2017 analysed various measurements in south-east USA and observed STT influence which can be seen to affect surface ozone levels. In their work they use various measurements from different instruments to give the structure and temporal evolution of ozone and the local weather system.

Ozone transported to the troposphere from the stratosphere can occur through diffusion (relatively slowly), or direct mixing. Intrusions of stratospheric air into the

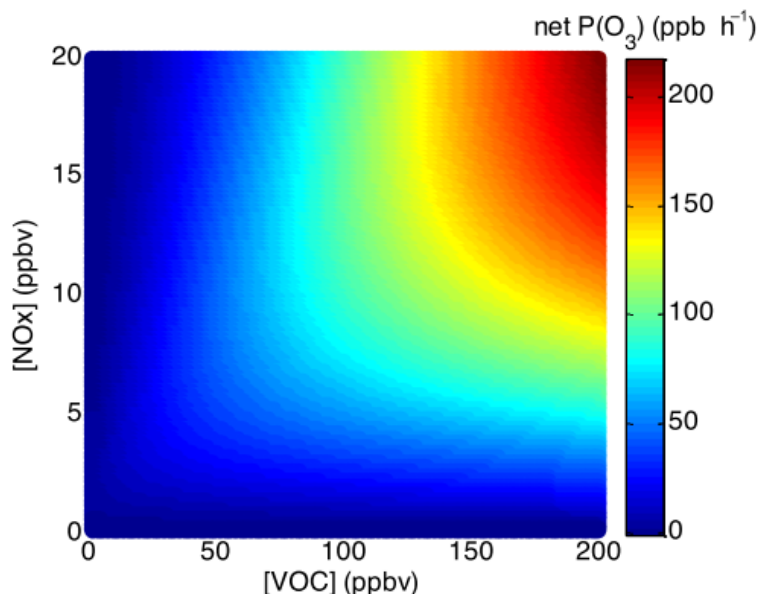
troposphere are often called Stratosphere to Troposphere Transport events (STT). STT often occur as tongues of stratospheric air descend and get disconnected from the stratosphere, potentially due to low pressure systems and jet streams Sprenger, Croci Maspoli, and Wernli, 2003. Recently global chemical transport models (CTMs) have been used to trace how much ozone is being transported to the troposphere from the stratosphere. There are a few methods of doing this, such as Ojha et al., 2016, who use the ECHAM5 CTM with a tracer that keeps track of ozone formed and transported from the stratosphere. Model based estimates generally require validation against actual measurements, such as those from ozonesondes or satellites. Hegglin and Shepherd, 2009 estimate that climate change will lead to increased STT due to an acceleration in the Brewer Dobson circulation. They estimate  $\sim 30$ , and  $\sim 121 \text{ Tg yr}^{-1}$  increases (relative to 1965) in the southern and northern hemispheres respectively

Liu et al., 2017 examine southern hemispheric ozone and the processes which control its inter-annual variability (IAV). IAV is the standard deviation of ozone anomalies from the monthly mean. They show that ozone transported from the stratosphere plays a major role in the upper troposphere, especially over the southern Indian ocean during austral winter. While stratospheric transport mostly impacts the upper troposphere, some areas are impacted right down to the surface. Liu et al., 2017 look at modelled tropospheric ozone sensitivity to changes in stratospheric ozone, ozone precursor emissions, and lightning over the southern hemisphere from 1992–2011. Their work suggest ozone at 430 hPa is mostly stratospheric in September over  $20^{\circ}\text{S}$  to  $60^{\circ}\text{S}$  at all longitudes. They also see tropospheric ozone sensitivity to emissions from South America ( $0\text{--}20^{\circ}\text{S}$ ,  $72.5\text{--}37.5^{\circ}\text{W}$ ), southern Africa ( $5\text{--}10^{\circ}\text{S}$ ,  $12\text{--}38^{\circ}\text{E}$ ), and South to Southeast Asia ( $70\text{--}125^{\circ}\text{E}$ ,  $10^{\circ}\text{S}\text{--}40^{\circ}\text{N}$ ). In the USA recent work by Lin et al., 2015 suggests that intrusions during spring are increasing surface ozone levels. Their work also recommends that understanding of frequency and cause of STT needs to be improved to effectively implement air quality standards.

### 1.2.2 Chemical production

An analysis of the Atmospheric Chemistry and Climate Model Inter-comparison Project (ACCMIP) simulations by Young et al., 2013 found STT is responsible for  $540 \pm 140 \text{ Tg yr}^{-1}$ , equivalent to  $\sim 11\%$  of the tropospheric ozone column, with the remainder produced photochemically (Monks et al., 2015). A recent summary by Young et al., 2017 estimates ozone production and loss in the troposphere to be  $\sim 4900 \text{ Tg yr}^{-1}$ , and  $\sim 4500 \text{ Tg yr}^{-1}$  respectively, while STT sources are  $\sim 500 \text{ Tg yr}^{-1}$ . They also show how all these figures are still relatively uncertain.

tropospheric ozone concentrations rely on climate and ozone precursor emissions; including NO, NO<sub>2</sub>, CO, VOCs, and HCHO (Atkinson, 2000; Young et al., 2013; Marvin et al., 2017). Ozone predictions are uncertain due to the vagaries of changing climate which affects both transport, deposition, destruction, and plant based precursor emissions. All of these processes are tightly coupled and difficult to accurately model, as they depend on uncertain assumptions such as CO<sub>2</sub> dependency (Young et al., 2013). Even with all the work done over the prior decades there remains large uncertainties about ozone precursors in the troposphere (Mazzuca et al., 2016).



**Figure 1.** Ozone production empirical kinetic modeling approach (EKMA) diagram using box model results with NO<sub>x</sub> levels varying from 0 to 20 ppbv and VOC levels from 0 to 200 ppbv. The mean concentrations of other species and the speciation of NO<sub>x</sub> and VOCs observed during DISCOVER-AQ in Houston in 2013 were used to constrain the box model. This diagram clearly shows the sensitivity of ozone production to NO<sub>x</sub> and VOCs in Houston.

FIGURE 1.3: Ozone production figure copied from Mazzuca et al., 2016.

Ozone is formed in the troposphere through oxidation of VOCs (described in Section 1.3)) in the presence of NO<sub>x</sub>. Net formation or loss of O<sub>3</sub> is determined by interactions between VOCs, NO<sub>x</sub>, and HO<sub>x</sub>, and is a complicated system of positive and negative feedbacks (Atkinson, 2000). Figure 1.3 shows the non-linear affect of NO<sub>x</sub> and VOC concentrations on ozone production over Houston, as modelled in Mazzuca et al., 2016. Recently the relationship has been examined on the intradiel timescale showing that ozone production can be more or less sensitive to VOCs at different hours depending on location various other factors (Mazzuca et al., 2016).

Ozone in rural areas is often higher than in populous cities, as the high NO levels titrate the O<sub>3</sub>. Equation 1.2 shows how NO and O<sub>3</sub> lead to NO<sub>2</sub> and the very short lived NO<sub>3</sub> radical.

Tropospheric ozone is lost via chemical destruction and dry deposition, estimated to be  $4700 \pm 700 \text{ Tg yr}^{-1}$  and  $1000 \pm 200 \text{ Tg yr}^{-1}$ , respectively (Stevenson et al., 2006; Young et al., 2017). The main loss channel is through equation 1.1, where photolysis and pressure create OH from the O<sub>3</sub>.

### 1.3 VOCs

Organic compounds are members of a large class of chemicals whose molecules contain carbon, with the exception of a few compounds such as carbides, carbonates ( $\text{CO}_3$ ), and simple oxides of carbon and cyanides. Organic compounds can be categorised based on their vapour pressure, which is the tendency of a liquid or solid to vaporise. Compounds with high vapour pressures at standard temperature are classed as volatile, and have a tendency to evaporate at low temperatures. Plants contain tens of thousands of organic compounds, it's likely that fewer than 40 are emitted due to the low volatility of most of them (Guenther et al., 2000).

Atmospheric organic compounds are legion and differ by orders of magnitude with respect to their fundamental properties, such as volatility, reactivity, and cloud droplet formation propensity, etc. Volatile organic compounds (VOCs) have vapour pressure greater than  $10^{-5}$  atm, and are mostly generated naturally by plants, which emit around  $1000 \text{ Tg yr}^{-1}$  (Guenther et al., 1995; Glasius and Goldstein, 2016). Due to their high volatility these compounds are generally seen in the gas phase. Organic compounds with a lower volatility are classed as semi-volatile (SVOCs: vapour pressure between  $10^{-5}$  and  $10^{-11}$  atm) are seen in both gas and particle phase depending on temperature and pressure. Organic compounds with even lower vapour pressure are generally found in the particle phase in aerosol particulate matter (Glasius and Goldstein, 2016). Understanding the drivers of trends in biogenic VOC emissions (BVOCs) is needed in order to estimate future carbon fluxes, changes in the water cycle, air quality, and other climate responses (Yue, Unger, and Zheng, 2015). In the last 20 years anthropogenic emissions of VOCs have been increasing while biogenic VOC emissions have decreased, due to rapid economic growth and lower annual temperatures (Stavrakou et al., 2014; Kwon et al., 2017).

VOCs are an important driver of atmospheric processes, especially near forests. VOCs are broken down into HCHO,  $\text{O}_3$ ,  $\text{CO}_2$  and various other species, mainly through oxidation (by OH). VOC emissions result in radical cycling, acid deposition, production of tropospheric ozone, and secondary organic aerosols (SOAs) (Atkinson, 2000; Kanakidou et al., 2005). A regional-model study in Europe (Aksoyoglu et al., 2017) has also shown VOCs impact secondary inorganic aerosol concentrations. These have impacts on climate (through radiative forcing) and air quality, affecting both human health and crop yields (Forster et al., 2007; Avnery et al., 2013; Lelieveld et al., 2015).

The major source of VOCs in the atmosphere is biogenic, with around 90% of emissions (globally) coming from natural sources (Guenther et al., 1995; Guenther et al., 2006; Millet et al., 2006). Methane ( $\text{CH}_4$ ) is one of the more abundant and potent VOCs, however it is often classified separately and compared against non-methane VOCs (NMVOCs). NMVOCs are alkanes, alkenes, aromatic hydrocarbons and isoprene, with isoprene being the most prominent. Methane and isoprene each comprise around a third of the global total emissions of VOCs (Guenther et al., 2006). However, methane is relatively long lived (years) and is well mixed in the atmosphere while isoprene levels are very volatile and spatially diverse due to a life time of around an hour. In this thesis I work towards a better understanding of the NMVOC emissions coming from Australia.

VOCs are removed by wet and dry deposition, OH oxidation, reaction with  $\text{NO}_3$ , ozonolysis (at night time or in polluted areas) or photolysis (Atkinson and Arey, 2003;

Brown et al., 2009). The process of deposition only accounts for a small fraction of the VOC loss, with the possible exception of the long lived methane compound (Atkinson and Arey, 2003).

PM in the atmosphere is a major problem, causing an estimated 2-3 million deaths annually (Hoek et al., 2013; Krewski et al., 2009; Silva et al., 2013; Lelieveld et al., 2015). Aerosols are suspended particulates and liquid compounds in the atmosphere, of which particulate matter (PM) is an important subset. Fine particulate matter ( $PM_{2.5}$ ) penetrates deep into the lungs and is detrimental to human health. Some PM comes from small organic aerosols (OA) emitted in the particulate phase and referred to as primary OA (POA). A substantial amount of PM is due to gaseous organic compounds transforming in the troposphere leading to what's known as secondary OA (SOA) (Kroll and Seinfeld, 2008).

Formation of SOA is generally due to VOC oxidation and subsequent reactions, while removal from the atmosphere is largely due to wet or dry deposition, and cloud scavenging (Kanakidou et al., 2005). It can be difficult to attribute PM formation, in part due to the complex relationship between  $NO_X$ , OH,  $O_3$ , and the uncertainty surrounding precursor emissions. Improved concentration estimates of these organic compounds requires a better understanding of their emissions, which is one of the foci in this thesis.

### 1.3.1 Isoprene

Isoprene, or 2-methylbuta-1,3-diene, is a VOC with the chemical formula  $C_5H_8$ . It is of major importance to the atmosphere, as it is involved in various processes which alter the oxidative capacity of the atmosphere. Guenther et al., 1995, and subsequent updates (Guenther et al., 2000; Guenther et al., 2006; Guenther et al., 2012), have been used ubiquitously by the atmospheric community as a global estimate of isoprene emissions, at roughly  $500-600 \text{ Tg yr}^{-1}$ , emitted mostly during the day. Recently an estimate of global isoprene emissions has been made using a completely different model, of around  $465 \text{ Tg C yr}^{-1}$ , by Messina et al., 2016 using ORCHIDEE. The global emission factors model used to derive both these estimates is based on modelling emissions from different plant species (phenotypes), and relatively few Australian species are used when forming in these estimates.

Isoprene affects  $NO_X$  and  $HO_Y$  cycling, see for example formulae 1.1, 1.2. In the presence of  $NO_X$ , isoprene forms tropospheric ozone and SOAs (Wagner, 2002; Millet et al., 2006). It has a short lifetime during the day, roughly an hour due to OH oxidation (Atkinson and Arey, 2003).

Measurements of isoprene are often uncertain or difficult to make accurately. Kanakidou et al., 2005 summarised how chamber experiments used to measure isoprene reactions may be unsuitable for comparison to the natural atmosphere. In Nguyen et al., 2014 many scientists and groups worked together on chamber measurements, to improve understanding of ambient atmospheric oxidation mechanisms of biogenic hydrocarbons (such as isoprene).



### 1.3.2 Emissions

Isoprene emissions are often classified as either anthropogenic, biogenic, or pyrogenic. The natural or biogenic sources are roughly ten times higher than the anthropogenic VOC sources (Guenther et al., 2006; Kanakidou et al., 2005). Major emitters are tropical broadleaves (notably eucalypts), and scrubs (Guenther et al., 2006; Arneth et al., 2008; Niinemets et al., 2010; Monks et al., 2015). TODO: why do plants emit? Emissions are affected by various factors such as temperature, sunlight, soil moisture, etc.

It used to be thought that emissions of anthropogenic and biogenic VOCs (AVOCs, BVOCs respectively) were roughly similar (Müller, 1992, TODO: more cites). In the 1990's it became clear that biogenic emissions of VOCs were in fact dominant, although methane emissions are still largely anthropogenic. Global NMVOC levels are estimated at 85 %, 13 %, and 3 % from biogenic, anthropogenic, and pyrogenic sources respectively (Kanakidou et al., 2005; Kefauver, Filella, and Peñuelas, 2014).

The World Meteorological Organisation (WMO) estimated that we are emitting 360 Mt yr<sup>-1</sup> of methane, compared to biogenic emissions of around 200 Mt yr<sup>-1</sup> (Atkinson, 2000). In 1995 emissions of other VOCs were estimated at 1150 Tg C yr<sup>-1</sup> from biogenic sources, and 100 Tg C yr<sup>-1</sup> from anthropogenic sources (Guenther et al., 1995; Atkinson, 2000). The main non-methane BVOC emissions are isoprene (44%) and monoterpenes (11%) (Guenther et al., 2000; Kefauver, Filella, and Peñuelas, 2014). Land use changes can drastically affect isoprene sources, for instance in the tropics where large scale deforestation has converted forest into crop lands (Kanakidou et al., 2005).

Biogenic VOC emissions affect surface pollution levels, potentially enhancing particulate matter (PM) and ozone levels.

Isoprene is emitted and enters the atmosphere in the gas phase, where it reacts with various chemicals, forming many new chemicals with reactions at various time scales. One common compound which is produced by these reactions is HCHO, which is easier to measure and often used to estimate how much isoprene is being emitted. There are many reactions which occur and are important to capture in models due to their impacts on air quality and physical properties in the lower atmosphere. The many children processes and products which begin with isoprene oxidation are often called the isoprene (photochemical) cascade Paulot2012; Crounse et al., 2012; Wolfe et al., 2016.

### 1.3.3 The isoprene cascade

Isoprene forms many products with various lifetimes, here I will present an overview of some important mechanisms and products which are useful to my work.

Photolysis and oxidation of many VOCs initially form alkyl radicals ( $\dot{R}$ ). Alkenes (VOCs with double bonded carbon, such as isoprene) react with ozone leading to organic peroxy radicals ( $RO\dot{O}$ ). These go on to form many products and lead to (amongst other things) aerosol, formaldehyde, and ozone formation, depending on various other factors such as sunlight and NO pollution (Atkinson, 2000).

## Oxidation

The primary first step for atmospheric isoprene is photooxidation, reacting with OH to form isoprene hydroxyperoxy radicals (RO $\dot{O}$ ) (Patchen2017; Wolfe et al., 2016; Marvin et al., 2017). There is still uncertainty about which pathways are most important following RO $\dot{O}$  production: HO $_2$  reactions predominantly produce hydroxyhydroperoxides (ISOPOOH), NO reactions largely produce methyl vinyl ketone (MVK) and methacrolein (MCR), and RO $_2$  reactions are also possible Liu et al., 2016b.

The first step in oxidising alkenes (including isoprene) is a replacement by OH of a double bond, as summarised by the equation from PATCHEN et al., 2007:  $R-CH=CH-R' + OH \longrightarrow R-CH(OH)CH-R'$  where R and R' represent hydrocarbons. This OH adduct then reacts with O $_2$  to produce a hydroxyperoxy radical (RO $\dot{O}$ ), which for isoprene can be any of six different isomers (PATCHEN et al., 2007). These RO $\dot{O}$  (also called organic-peroxy/alkyl-peroxyl/ISOPOO radicals, or RO $_2$ ) react with HO $_2$  or NO and produce stable products (often called oxidised VOCs or OVOCs) (Nguyen et al., 2014). The RO $\dot{O}$  react with various compounds including NO, HO $_2$  and other RO $\dot{O}$ , with most pathways potentially producing HCHO (Wolfe et al., 2016).

This is where the isoprene oxidation path splits depending on the NO $_x$  concentration. Reactions with NO can lead to ozone production in environments rich in isoprene or other non-methane organic compounds (NMOCs) and NMVOCs (PATCHEN et al., 2007; Atkinson and Arey, 2003). These reactions are complex and coupled, for example NO $_2$  concentrations can be increased by NMOC and NO reactions (Atkinson and Arey, 2003). In the presence of NO $_x$ , the RO $\dot{O}$  may form organic nitrates after reacting with NO. Any organic nitrates which are formed affect levels of both HO $_x$  (H, OH, peroxy radicals) and NO $_x$ , acting as a sink (Mao et al., 2013 and references therein).

Reaction with NO $_2$  forms isoprene nitrates, or hydroxynitrate (RONO $_2$ ). The first generation of organic nitrates produced by isoprene oxidation range from 7% to 12%, shown in laboratory experiments (Paulot et al., 2009a; Mao et al., 2013). A portion of isoprene nitrates are recycled back to NO $_x$ , so may serve as a reservoir of nitrogen and allow its transport to the boundary layer of remote regions (PATCHEN et al., 2007; Paulot et al., 2009a). The nitrates can also build up in the winter, when removal processes are not as dominant (Lelieveld et al., 2009). NO $_x$  is removed primarily by conversion to nitric acid (HNO $_3$ ) followed by wet or dry deposition (Ayers and Simpson, 2006).

Oxidation reactions are important and quickly stabilise the ratio of NO to NO $_2$ . There is still large uncertainty around the fate of various RO $\dot{O}$ , which limits understanding of the relative importance of some chemical processes (Crounse et al., 2013).

Some portion of emitted isoprene leads to SOA, potentially through the formation of methacrylic acid epoxide (MAE) formed by decomposition of methacryloylperoxynitrate (MPAN, a second generation product of isoprene oxidation) as shown in smog chambers and field studies in Lin et al., 2013.

Isoprene oxidation by OH is less well understood when lower concentrations of NO are present in the atmosphere. Initially isoprene was thought to be a sink for atmospheric oxidants (e.g. Guenther et al., 2000). It was thought that in low NO environments, like those far from anthropogenic pollution and fires, oxidation of isoprene would create ISOPOOH and lead to low concentrations of OH and HO $_2$  Paulot et al.,

2009b. In Paulot et al., 2009b, the  $\text{HO}_x$  levels are shown to be largely unaffected by isoprene concentrations. They show that ISOPOOH is formed in yields  $> 70\%$ , and MACR and MVK is formed with yields  $< 30\%$ . The formation of MACR and MVK produces some  $\text{HO}_x$ , although not enough to close the gap. Paulot et al., 2009b goes on to suggest (and provide experimental evidence) that dihydroxyperoxides (IEPOX) are formed from oxidation of the ISOPOOH, which form precursors for SOAs as well as closing the  $\text{HO}_x$  concentration gap. They then use GEOS-Chem, modified to include IEPOX formation, to estimate that one third of isoprene peroxy radicals react with  $\text{HO}_2$ , and two thirds react with NO. They estimated  $95 \pm 45 \text{ Tg yr}^{-1}$  IEPOX being created in the atmosphere, which (at the time) was not modelled by CTMs. Their work showed another pathway for isoprene based SOA creation, through these IEPOX creation and  $\text{HO}_x$  recycling mechanisms. Peeters and Muller, 2010 suggested that the work of Paulot et al., 2009b only partially bridges the gap between clean air OH concentration measurements and models. They suggested four new mechanisms for OH recycling in these pristine conditions. These can be summarised as OH regenerating reactions which occur during photolysis of hydroperoxy-methyl-butenals (HPALDs), and resulting photolabile peroxy-acid-aldehydes (PACALDs). These reactions are highly non-linear and subject to large uncertainty, however when compared against several campaigns they were shown to improve one particular models (IMAGES)  $\text{HO}_x$  concentrations. In Crounse et al., 2012, MACR products are examined in various conditions and hydroxy recycling is also observed in low NO conditions.

Although understanding of OH production/recycling in these low NO conditions has been improved, many observations of OH were still quite under-predicted in models (Mao et al., 2012). Mao et al., 2012 showed how traditional OH measurements may be overestimated due to VOC oxidation. They looked at measurements in a remote forest in California and found that the instruments were generating OH internally. Nguyen et al., 2014 also see this VOC oxidation interference in measurements using a gas chromatographer (GC) with an equipped flame ionisation detector (FID). This lends more credence to the current understanding of VOC oxidation as it closed the gap between measurements and model predictions (Mao et al., 2012).

Peeters and Muller, 2010 showed that  $\text{HO}_2$  is produced at near unity yields following isoprene oxidation initiated by OH. TODO: read more Peeters2010

Nguyen et al., 2014 examine various measurement techniques to determine isoprene reactions in non-laboratory conditions. Their work discussed how large uncertainties persist in isoprene oxidation, which carries through to predictions by atmospheric models. Nguyen et al., 2014 show preliminary estimates of low-NO yields of MVK and MCR to be  $6 \pm 3\%$  and  $4 \pm 2\%$  respectively, consistent with TODO:Liu2013 but only when cold-trapping methods are employed. These yields each increase (due to interference by OVOCs) to greater than 40% when directly sampled by GC-FID.

Even with the recent boom in isoprene analysis, uncertainties remain in the isoprene oxidation mechanisms. Examples (taken from Nguyen et al., 2014) include isoprene nitrate yields, which range from 4-15% (Paulot et al., 2009a), 90% disagreements in MAC and MVK yields TODO:(Liu2013), various possible sources for SOA TODO:(Chan2010; "Reactive intermediates revealed in secondary organic aerosol formation from isoprene"; Lin et al., 2013), unknown HPALD fates, incomplete  $\text{O}_2$  incorporation TODO:(Peeters2009; Crounse et al., 2013), and under-characterized  $\text{RO}_2$



lifetime impacts TODO:(Wolfe2012). TODO: get those citations and read abstracts.

### Ozonolysis

Ozonolysis is the splitting of carbon chains by ozone molecules, and is among the primary oxidation pathway for volatile alkenes (Nguyen et al., 2016). Criegee intermediates (carbonyl oxides with two charge centres) are formed when isoprene reacts with  $O_3$ . Nguyen et al., 2016 examine in detail a few of these, with proposed mechanisms for  $C_1$  and  $C_4$  Criegee intermediate reactions. The  $C_1$  stabilised Criegee ( $CH_2OO$ ,  $\sim 61\%$ ) is therein proposed to react with water yielding 73% hydroxymethyl hydroperoxide (HMHP), 6%  $HCHO + H_2O_2$ , and formic acid +  $H_2O$ , and the same products with yields of 40, 6, and 54% respectively when this Criegee reacts with  $(H_2O)_2$ . TODO: more on Nguyen2016?

### Oxidation by $NO_3$

At night when OH concentrations have dropped, isoprene can remain in the atmosphere to be transported. Typically less than half of this night time isoprene is removed through ozonolysis (Atkinson and Arey, 2003), however, in polluted areas where high levels of  $NO_x$  exist, isoprene is consumed by a different radical. During the night isoprene is oxidised by nitrate radicals ( $NO_3$ ), which joins to one of the double bonds and produces organic nitrates in high yield (65% to 85%) (Mao et al., 2013). (todo: read mao2013 para 3 cites)  $NO_3$  are largely formed through ozone reactions, as in equation 1.2. A build up of  $NO_3$  radicals can be seen at night, when photolysis is not removing them quickly (Atkinson, 2000; Brown et al., 2009).

In areas with high  $NO_x$  levels, greater than 20% of the isoprene emitted late in the day ends up being oxidised by the  $NO_3$  radical over night (Brown et al., 2009). At night isoprene has affects on both  $NO_x$  concentrations and ozone levels, and can form harmful organic nitrates and SOAs (Brown et al., 2009; Mao et al., 2013). These nitrates go on to produce further SOAs, largely due to  $NO_3$  reacting with first generation isoprene oxidation products (Rollins et al., 2009). The night-time concentrations of OH and ozone also have a complex effect on  $NO_x$  removal in high latitude winters, when photolysis and NO reactions are reduced (Ayers and Simpson, 2006).

Rollins et al., 2009 examine SOA production in a large chemical reaction chamber, over 16 hr in the dark and find first generation mass yield ( $\Delta SOA \text{ mass} / \Delta \text{isoprene mass}$ ) to be less than 0.7%, with further oxidation of initial products (isoprene reacting twice with  $NO_3$ ) yielding 14%. This led to an overall mass yield of 2% over the 16 hr experiment. Night  $NO_3$  levels also affect  $O_3$ , TODO: millet et al 2016.

#### 1.3.4 Radiative Forcing

Gas phase emissions with higher vapour pressures can be oxidised into lower vapour pressure products which will partition between gas and particle phase, often called semi or non-volatile. The aerosol products from these gas phase emissions (or the children thereof) are SOA (Kanakidou et al., 2005).

One of the large uncertainties with OA is the total effect on radiative forcing, 12 years ago it was well understood that most OA cool the atmosphere, with smaller

particles having a larger affect due to the size matching the wavelengths of visible light (Kanakidou et al., 2005). Transport and indirect effects complicate matters further, with cloud creation and modification of cloud properties being quite difficult to accurately predict. In the third IPCC report (*Intergovernmental Panel on Climate Change (IPCC): Climate Change: The Scientific Basis* 2001), the uncertainty involved if OA forcing was a factor of 3 times the estimated effect. This has since been improved however OA and cloud formation still remains a large uncertainty in more recent IPCC reports (Forster et al., 2007). Figure 1.4 shows the radiative forcing (RF) of various atmospheric constituents, it's clear that OA uncertainty dominates. Figure 1.5 shows the same summary updated in chapter 8 of the fifth report, where the SOA uncertainty remains quite large. It's currently understood that SOA plays an indirect and complex role in cloud properties, with a net cooling effect (*IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, Chapter 7,8)

Kanakidou et al., 2005 highlight the need for improving emissions and flux measurements, in addition to utilising satellite data in models as a means of improving the emissions inventories. Observed nucleation outside of laboratories can arise from biogenic SOAs, driven by ozonolysis. Kanakidou et al., 2005 concluded that it is very likely that organics contribute to particle growth and formation rates.

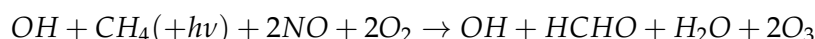
## 1.4 HCHO

One of the major products of isoprene chemistry is HCHO. HCHO is important both for its own sake, and as a proxy for determination of isoprene emissions. Using the estimated yield of HCHO from precursor emissions allows us to estimate these precursors.

HCHO, aka methanal, methyl aldehyde, or methylene oxide, is of the aldehyde family. HCHO is an OVOC which is toxic, allergenic, and a potential carcinogen. It is dangerous at low levels, with WHO guidelines for prolonged exposure at 80 ppb. HCHO is used as an adhesive in plywood, carpeting, and in the creation of paints and wallpapers. Emissions in enclosed spaces can build up to dangerous levels, especially if new furnishings are installed (Davenport et al., 2015). At global scales HCHO in furniture is less important, as concentrations are driven by photochemical reactions with methane and other VOCs.

### 1.4.1 Sources and sinks

Background levels of HCHO in the atmosphere are driven by the oxidation of methane ( $\text{CH}_4$ ) by the hydroxyl radical ( $\text{OH}^{-1}$ ). Atkinson, 2000 summarised the background formation of HCHO with the following reaction:



which shows that photolysis and oxidation of methane forms HCHO and ozone in a process that regenerates the OH radicals.  $\text{CH}_4$  concentrations are thought to be well constrained in models, with the ACCMIP comparison showing only  $\sim 3\%$  inter-quartile range (Young et al., 2013). There is a complex relationship between VOCs,

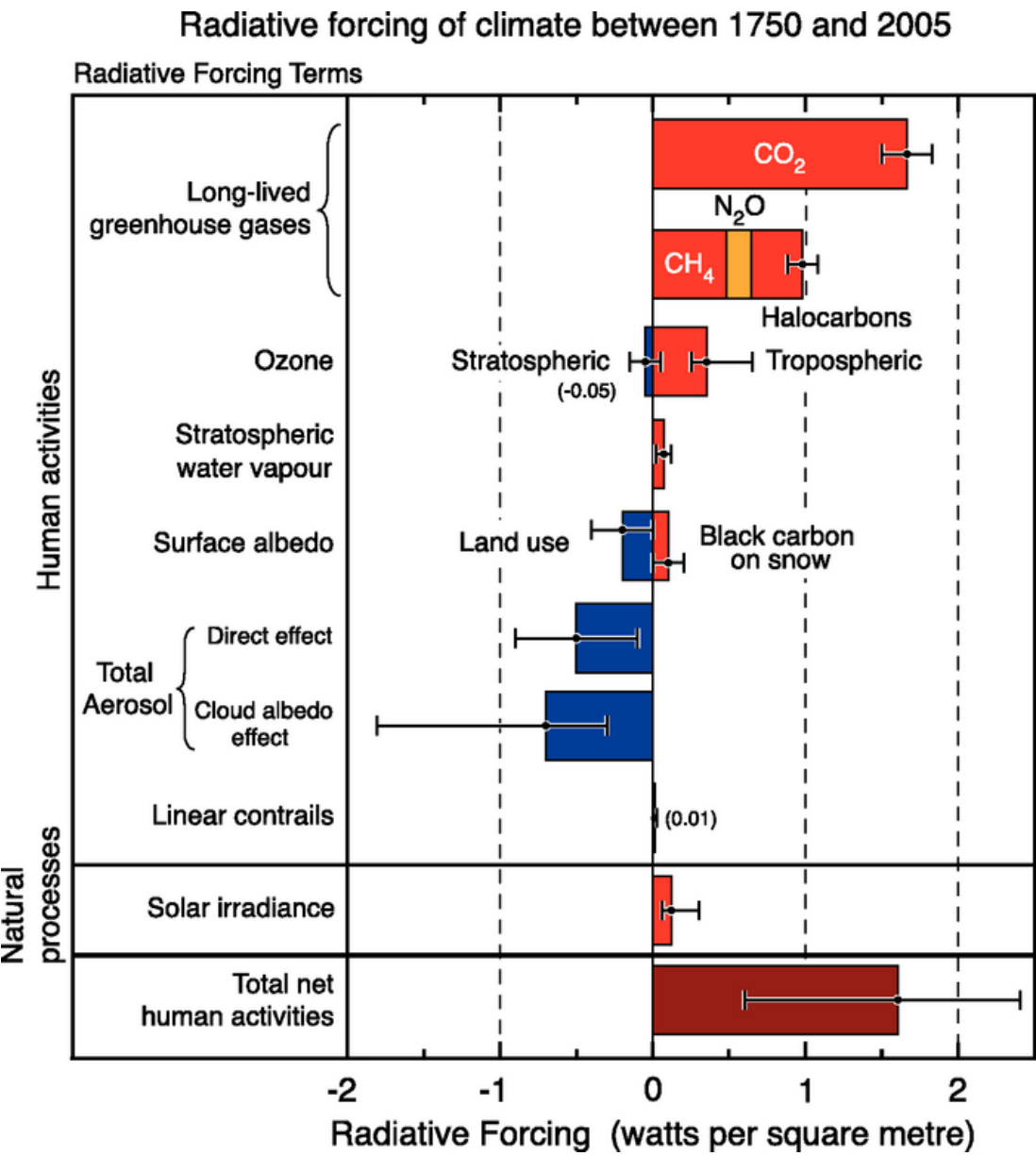
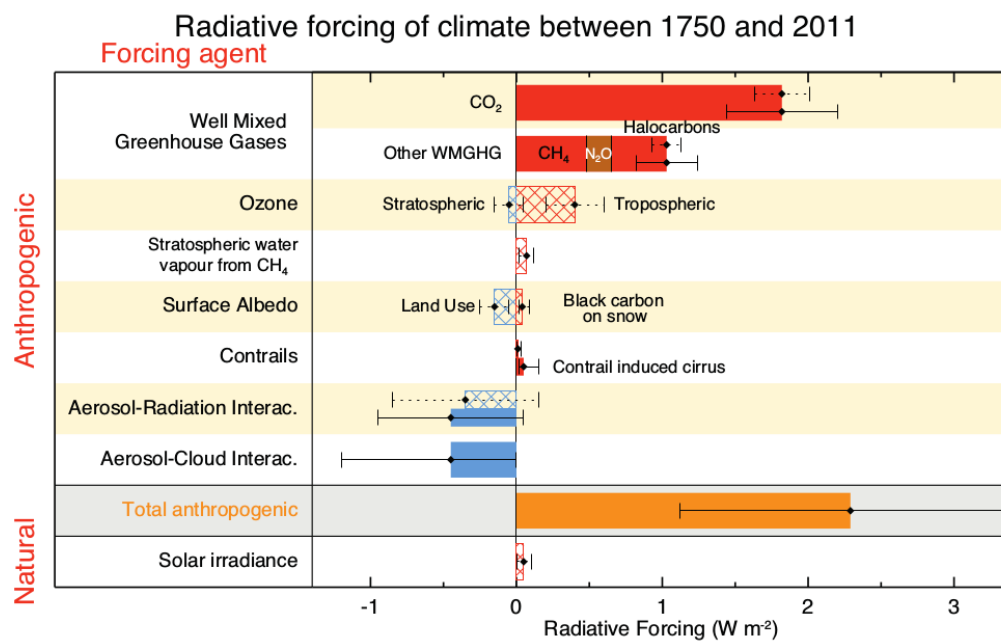


FIGURE 1.4: The overall radiative forcings and uncertainties of several atmospheric constituents This is an image taken from Forster et al., 2007, found at [https://www.ipcc.ch/publications\\_and\\_data/ar4/wg1/en/faq-2-1.html](https://www.ipcc.ch/publications_and_data/ar4/wg1/en/faq-2-1.html).



**Figure 8.15** | Bar chart for RF (hatched) and ERF (solid) for the period 1750–2011, where the total ERF is derived from Figure 8.16. Uncertainties (5 to 95% confidence range) are given for RF (dotted lines) and ERF (solid lines).

FIGURE 1.5: The overall radiative forcings and uncertainties of several atmospheric constituents This is an image taken from *IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, chapter 8.

HO<sub>x</sub>, and NO<sub>x</sub>, and with higher levels of NO<sub>x</sub> the speed that VOCs are converted into HCHO increases, as does the HCHO concentration (Wolfe et al., 2016).

Within the continental boundary layer, the major source of HCHO enhancement is VOC emissions reacting with OH radicals in the presence of NO<sub>x</sub> (Wagner, 2002; Millet et al., 2006; Kefauver, Filella, and Peñuelas, 2014). Enhancements to regional and continental HCHO are largely driven by isoprene emissions (Guenther et al., 1995; Palmer, 2003; Shim et al., 2005; Kefauver, Filella, and Peñuelas, 2014). This is true except near fires or anthropogenic sources of HCHO and precursors (Guenther et al., 1995; Kefauver, Filella, and Peñuelas, 2014; Wolfe et al., 2016). Biomass burning (BB) can be a source of HCHO, and various other pollutants, precursors, and aerosols (Guenther et al., 1995; Andreae, 2001). Additionally HCHO is emitted into the atmosphere directly through fossil fuel combustion, natural gas flaring, ethanol refining, and agricultural activity (Wolfe et al., 2016).

Other terpenoids (monoterpenes, sesquiterpenes, etc.) can also produce HCHO, although generally to a lesser extent than isoprene, methane and biomass burning (Guenther et al., 2012). Many of the HCHO yields from terpenoids are estimated through chamber studies which examine the products molecular mass and charge after mixing the compound of choice into a known volume of air (Nguyen et al., 2014, eg.). These conditions generally don't match those of the real world, where ambient air will have a cocktail of these compounds as well as various reactants. Nguyen et al., 2014 state that one of their goals is to recreate ambient atmosphere in their chamber studies with more accuracy, in order to improve interpretations and allow more accurate model parameters.

Millet et al., 2008 show that anthropogenic emissions of HCHO in America are mostly negligible, although improved sensitivity from oversampling allowed satellite detection of enhanced HCHO concentrations over Houston and Texas (Zhu et al., 2014). This is not the case in China, since massive population centres and industrial districts are emitting huge amounts of VOCs into the atmosphere (Fu et al., 2007). Fu et al., 2007 use GOME measurements over Asia and derive biogenic, anthropogenic, and pyrogenic VOC emissions, and Zhu et al., 2014 use oversampling of the OMI HCHO measurements to determine anthropogenic highly-reactive VOC emissions. Then with their updated emissions they show how surface ozone is affected, with a seasonal increase of 5-20 ppb simulated by GEOS-Chem.

In the past, HCHO levels were underestimated by models, often with large discrepancies, due to the poor understanding of methyl peroxy radical (CH<sub>3</sub>OO) chemistry (Wagner, 2002). Nowadays HCHO concentrations are better understood, however precursor emissions are one of the main unknowns (Emmerson et al., 2016; Marvin et al., 2017, eg.). Marvin et al., 2017 found that discrepancies in modelled HCHO concentrations are primarily due to second and later generation isoprene oxidation chemistry.

HCHO has two major sinks, one being reactions with OH (oxidation), the other being photolysis: the process of being broken apart by photons (CRUTZEN, LAWRENCE, and PÖSCHL, 1999; Wagner, 2002; Levy, 1972; Kefauver, Filella, and Peñuelas, 2014). These reactions lead to a daytime lifetime of a few hours (Atkinson, 2000; Millet et al., 2006). Both these loss processes (photolysis, oxidation) form CO and hydroperoxyl

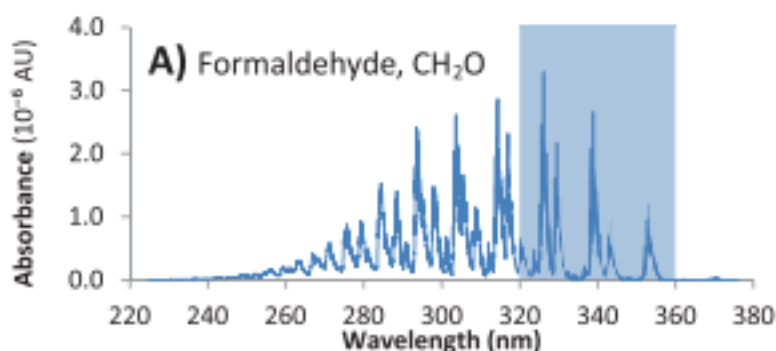


FIGURE 1.6: HCHO spectrum, with a typical band of wavelengths used for DOAS path measurements. This is a portion of an image from Davenport et al., 2015.

radicals ( $\text{HO}_2$ ), and have global significance to radiative forcing and oxidative capacity (Franco et al., 2015). The other notable sinks are wet and dry deposition, although these are not as significant (Atkinson, 2000) (TODO: add more cites here).

#### 1.4.2 Measurement techniques

There are a few ways to measure HCHO, including Fourier Transform Infra-Red Spectrometry (FTIR) and Differential Optical Absorption Spectroscopy (DOAS). FTIR examines the Fourier transform of a measured spectrum in order to determine what trace gases are interfering within the IR range of light. DOAS methods are based on light interference and absorption through air masses.

The DOAS technique takes advantage of the optically thin nature of HCHO in order to linearise the radiance differential through air masses with and without HCHO, using the Beer-Lambert intensity law. This method works for both in the home HCHO detection and global measurements from in-situ and remote sensing instruments (Guenther et al., 1995; Gonzalez Abad et al., 2015; Davenport et al., 2015). As a trace gas HCHO interferes with light over a few wavelength bands, which allows instruments to detect concentrations between a known light source and a detector. Figure 1.6 shows the interference spectrum of HCHO as well as a typical band used to examine interference in the DOAS technique. One difficulty is that this interference is relatively small (HCHO is optically thin) and other compounds absorb light at similar wavelengths (Davenport et al., 2015).

FTIR measurements can have a range of uncertainties, including systematic and random measurement errors and uncertain apriori shape factors and water profiles (eg: Franco et al., 2015). Other types of measurement involve directly measuring the air, and determining chemical compounds through their physical properties. A proton transfer reaction mass spectrometer (PTR-MS) can be used to determine gas phase evolution of terpene oxidation products (Lee et al., 2006; Nguyen et al., 2014; Wolfe et al., 2016, eg.). This is done through analysis of mass to charge ratios ( $m/z$ ) of ionised air masses which are then identified as chemical compounds. Nguyen et al., 2014 use and compare several instruments (including one which is PTR-MS based) in the



analysis of isoprene and monoterpene products. A Gas Chromatography mass spectrometer (GC-MS) is also able to identify isoprene, monoterpenes, and their products Nguyen et al., 2014, eg.

Other measurement techniques include chromatographic and fluorimetric methods, both of which differ widely from each other and the spectroscopic methods (Hak et al., 2005). Hak et al., 2005 examine a single air mass with 8 instruments using the four techniques (MAX-DOAS, FTIR, chromatographic, and fluorimetric), and show that reasonable agreements can be achieved. Generally the measurements were somewhat close, the five Hantzsch instruments agreeing to within 11% (after removing two potentially faulty measurements), although different calibration standards were used. Titration for the different calibration solutions could not be resolved, which may account for absolute offsets up to 30%. These differences and non-uniformities between measurements (even among identical instruments) are part of the reason HCHO does not have a consistent network for global measurements like those for GHGs or Ozone (Chevallier et al., 2012).

### Satellite measurements

Several satellites provide long term trace gas observations with near complete global coverage, including the ERS-2 launched in April 1995 which houses the GOME ultraviolet and visible (UV-Vis) spectrometer, the AURA launched in July 2004 which houses the OMI UV-Vis spectrometer, the MetOp-A and B launched in October 2006 and September 2012 respectively both housing a GOME-2 UV-Vis spectrometer. These satellites are on Low Earth Orbit (LEO) trajectories and overpass any area up to once per day. Satellites can use DOAS techniques with radiative transfer calculations on solar radiation absorption spectra to measure column HCHO. An example of a spectrum retrieved from the GOME-2 instrument is given in figure 1.7.

In conjunction with atmospheric chemistry and radiative models, satellite measurements can be used to quantify the abundance of several chemical species in the atmosphere. Isoprene is hard to measure directly due to its short lifetime and weak spectral absorption, instead HCHO is often used as a proxy (Millet et al., 2006; Fu et al., 2007; Dufour et al., 2008; Marais et al., 2012; Bauwens et al., 2013; Kefauver, Filella, and Peñuelas, 2014; Bauwens et al., 2016). This leads to a method of isoprene emissions estimation termed top-down (as opposed to bottom-up estimates like MEGAN). The existence of satellite data covering remote areas provides an opportunity to improve VOC emissions estimates leading to more robust models of global climate and chemistry. Satellite data allows us to verify large scale models of natural emissions, and their subsequent chemistry.

## 1.5 Atmospheric Chemistry Modelling

Models can fill the gaps (both spatial and temporal) in measurement records, and are used to predict/prevent/understand various scenarios. They are used ideally to steer us away from unsustainable pollution and help complete our understanding of the world from small to large scales. They can be used to increase measurement accuracy (for instance in satellite measurements) and determine where we lack information,

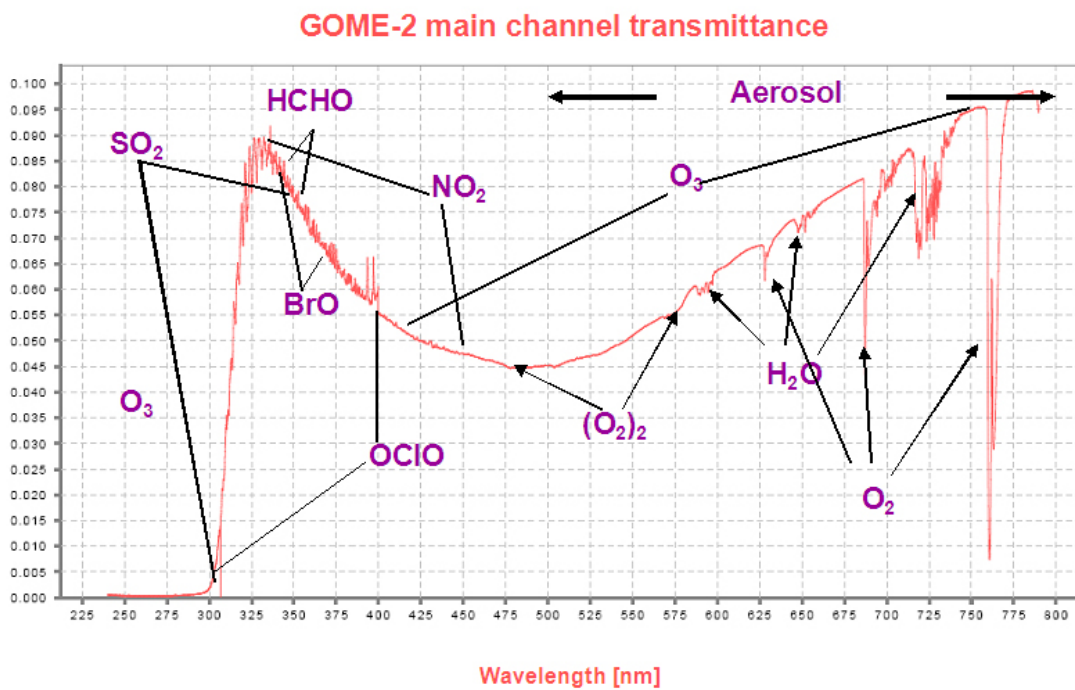


FIGURE 1.7: An example spectrum showing interferences used for species concentration measurements by GOME-2. Image by EUMETSAT and ESA (EUMETSAT, 2015).

)



while also checking the performance of new instruments. Precisely representing various chemicals and reactions in the atmosphere allows efficient mitigation of pollution, since we can compare scenarios against one another. Currently, improved isoprene understanding is critical for effective air quality measuring (Marvin et al., 2017).

Atmospheric chemical models provide a simulation of chemical densities and transport over time, through the atmosphere. They require various inputs in order to accurately represent scenarios or regions on earth. Models of emissions are often used as drivers for atmospheric chemistry models, which generally require initial and boundary conditions in order to run. The chemistry in the atmosphere is a complex system of coupled reactions and dynamics, and is generally solved using numerical partial differential equation solvers.

Chemical Transport Models (CTMs) simulate production, loss, and transport of chemical species. This is generally calculated using one or both of the Eulerian (box) or Lagrangian (puff) frames of reference. CTMs normally solve the continuity equations simultaneously with chemical production and loss for chemicals under inspection. The continuity equations describe transport of a conserved quantity such as mass, which, solved together with production and loss of a chemical can provide detailed simulations of natural processes.

The general continuity equation links a quantity of a substance ( $q$ ) to the field in which it flows and can be described by the formula:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot j = \sigma$$

where  $\rho$  is density of  $q$  in the field,  $t$  is time,  $\nabla$  is divergence,  $j$  is the flux ( $q$  per unit area per unit time entering or leaving the field), and  $\sigma$  is the generation or loss of  $q$  per unit volume per unit time.

The type of model best suited to modelling the entire earth uses the Eulerian frame of reference, where the atmosphere is broken up into 3-D boxes with densities and transport calculated and stored for sequential steps in time at each location. The mass balance equation must be satisfied in any realistic long term box model and is as follows:

$$\begin{aligned} \frac{dm}{dt} &= \sum sources - \sum sinks \\ &= F_{in} + E + P - F_{out} - L - D \end{aligned}$$

where  $m$  is mass of a chemical,  $E$  and  $D$  are emission and deposition,  $P$  and  $L$  are production and loss, and  $F$  is chemical transport in and out, as shown in figure 1.8. Many chemical species interact with each other through production and loss. Any large chemical model will solve this mass balance equation over highly coupled arrays of partial differential equations which can be complex and time consuming.

Contemporary models generally use mathematical differential solving tools of various complexity to solve chemical equations and reaction rates (often called chemical mechanisms) in order to predict an environments evolution over time. Different solvers may be slower or faster and more suited to particular situations based on the stability of the equations and systems involved, and chemical mechanisms may vary

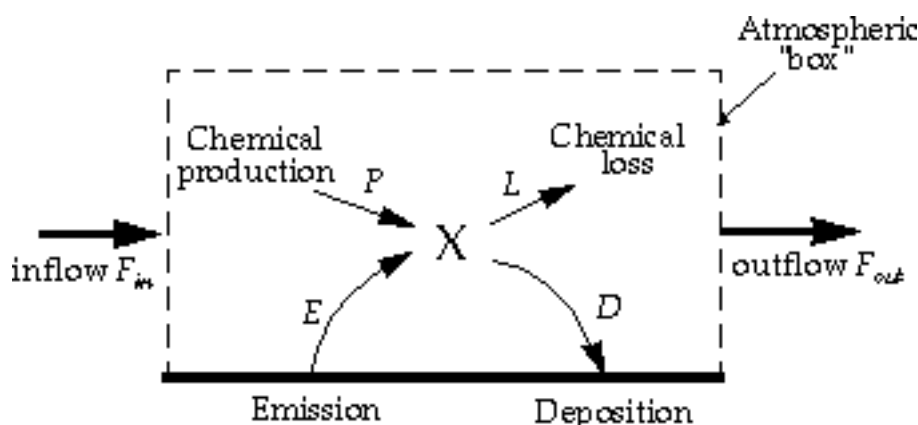


FIGURE 1.8: Standard box model parameters, image taken from Jacob, 1999.

in how many reactions and chemicals are listed and grouped together. For example: Since  $[O] \ll [O_3]$  the chemical family  $O_X$  ( $O_X \equiv O + O_3$ ) can be used to simplify chemistry simulations and approximate  $O_3$  concentrations (Brasseur and Jacob, 2017, Chapter 3). Zhang et al., 2012 examine the outputs from a regional model (WRF/Chem) using three different chemical mechanisms, and they show that particulate matter prediction is sensitive to the choice of chemical mechanism.

### 1.5.1 Box models

Box models are much smaller scale than global CTMs, examining one uniform environment with many parametrisations such as transport and emissions. Box models can be used to check chemical mechanisms in specific scenarios, such as high or low  $NO_X$  environments. Marvin et al., 2017 use a box model matching conditions in southeast USA to evaluate isoprene mechanisms from several models. A box model involves modelling chemistry in a singular set of conditions without transport or any spatial gradients. One box model used in this thesis is called CAABA/MECCA, and is described in Section ??.

By allowing for interactions between boxes this concept can be extended to multiple-box models. These are simply multiple instances of single boxes with the addition of transport between them, which generally requires a meteorological model to provide winds, and other transport mechanisms.

### 1.5.2 Emissions

There are two commonly used ways of estimating isoprene emissions, top-down or bottom-up. Bottom-up emission estimates generally model the flora and events which emit isoprene, like Eucalypts, factories, shrubs, etc. They use various properties of the emitters in order to estimate how much isoprene is being produced. Some of these properties include leaf areas, speciated responses to sunlight and temperature, moisture stress, etc (Guenther et al., 1995; Guenther et al., 2006). Understanding how much isoprene is emitted, when and by what, is complicated. Since little data exists with which to verify many of these bottom-up emission inventories, they can be uncertain

on a large scale. Emissions inventories such as MEGAN are bottom-up and use models of emissions based on tree types, weather, and other parameters.

In many CTMs the isoprene emissions are calculated separately (for example by running MEGAN), and then used as boundary conditions (EG: Guenther et al., 2006). This can speed up calculations as the transport and concentrations can be simulated in various conditions without recalculating the emissions. Trace gases with short lifetimes and complex chemistry such as isoprene are often hard to measure which makes verifying model estimates difficult.

Bottom up models of VOC emissions are sensitive to parameters. Stavrou et al., 2014 examined modelled Asian emissions and altered model parameters for temperature, plant type emission factors, incoming solar radiation (insolation) intensity, land use changes, and palm tree forest expansion. Changes were constrained by a network of radiation measurements and some experiments with south east Asian forest emissions - and led to reduction in isoprene emissions by a factor of two over the region. The Asian region is shown to have a strong correlation with the Oceanic Niño Index (ONI), with positive anomalies associated with El Niño.

Marais et al., 2014 examine factors affecting isoprene emissions, showing how emissions are sensitive to various environmental factors. Their work used MEGAN (Guenther et al., 1995) and GEOS-Chem to look at how these factors affect surface ozone and particulate matter in Africa. One of the important uncertainties seen in MEGAN within this work is the isoprene emissions due to plant type. Canopy level isoprene measurements are made using relaxed eddy accumulation (REA) at several sites in Africa. One plant type near a measurement site emits more than other species and its actual distribution on a larger scale is completely unknown - leading to possible overestimations in MEGAN. Current emissions estimates require more validation against observations, and recently a comparison of two major VOC models (MEGAN and ORCHIDEE) was undertaken by Messina et al., 2016 reiterating this requirement. In their work they examine model sensitivities and show that the important parameters are leaf area index (LAI), emission factors (EF), plant functional type (PFT), and light density fraction (LDF). There is high uncertainty in LAI and EF, which require more or improved measurements at the global scale. LDF parameterisation needs improvement and these models require more PFTs. Global emissions inventories like MEGAN suffer from large extrapolations which introduce uncertainties (Miller et al., 2014).

### 1.5.3 Uncertainties?

Here I will attempt to list and partially explain the major uncertainties models have in relation to VOCs, SOAs, and ozone. TODO: Is this a good idea or should I put any pertinent uncertainties with the associated work/descriptions?

#### Emissions Inventories

Using different emissions inventories in an ACM can have large impacts on the simulation. Natural (biogenic or pyrogenic) and human driven (anthropogenic) emissions often drive a large fraction of atmospheric oxidation and radical chemistry, especially in the continental boundary layer. Zeng et al., 2015 examine the affects on CO and

HCHO when running simulations with two different inventories. TODO: find where I took notes about Zeng2015 and put them here.

It is important to note that many estimates of isoprene emission are based on a few algorithms which can depend greatly on input parameters (Arneth et al., 2008; Niinemets et al., 2010). Arneth et al., 2008 argue that this monopoly of emissions estimates may be leading us to an incorrect understanding of isoprene chemistry. Yue, Unger, and Zheng, 2015 has shown that this is still a problem by looking at land carbon fluxes and modelling the sensitivity to VOC emissions estimates using two independent models of VOC emission. One model is photosynthesis based and estimates isoprene emissions using electron transfer energies and leaf physiology (Niinemets et al., 1999), while the other (MEGAN) uses the light and canopy temperature ((Guenther et al., 1995; Arneth et al., 2007) TODO: Read Arneth et al., 2007; Unger et al., 2013). Both are sensitive to light and temperature parameterisations.

Isoprene emissions estimates are still fairly uncertain, as global measurements are difficult and regional emissions can be very different. The global uncertainty of isoprene emission was estimated to be a factor of 2 to 5 (250-750 Tg yr<sup>-1</sup>) (Kanakidou et al., 2005). Improvements over the years have been incremental, and generally localised to regions of particular interest for air quality such as China and the USA TODO: find recent uncertainty estimate improvements examples. The lack of accuracy in BVOC emissions estimates prevents accurate determinations of the sources and distribution of pollutants including ozone and organic aerosols. Most of the tropospheric SOA comes from biogenic precursors, the evidence for this has grown over the last two decades (Guenther et al., 1995; Kanakidou et al., 2005; Guenther et al., 2012). Accuracy in VOC measurements is important: it has been shown that even the diurnal pattern of isoprene emissions has an effect on modelling ground level ozone (Hewitt et al., 2011; Fan and Zhang, 2004).

Improvements to emissions models require improved understanding of regions and their behaviour. Inaccuracies can arise due to lack of data, such as the large and sparsely measured Australian outback. MEGAN has been shown to overpredict isoprene and underpredict monoterpene emissions in southeast Australia, with peaks and troughs captured but not at the right magnitude (Emmerson et al., 2016). MEGAN output in Australia is adversely affected by poor emission factor estimation. An example can be seen in Müller et al. (2008) where MEGAN overestimates isoprene in northern Australia. Underestimates of monoterpenes may be due simply to underestimated emission rates for many Eucalypt species (Winters et al., 2009).

## Resolution

GEOS-Chem simulations are somewhat sensitive to the resolution at which you run. For example: Wild and Prather, 2006 show that reduced resolution increases OH concentrations and ozone production rates. Christian, Brune, and Mao, 2017 find small changes in OH (< 10%) in OH, HO<sub>2</sub> and ozone concentrations local to the north american arctic, when changing from 4 by 5 to 2 by 2.5 °resolution, however they continue at lower resolution to save computational time.

For many global scale analyses, errors from resolution are less important than those from chemistry, meteorology, and emissions (Christian, Brune, and Mao, 2017).

Many models lack in-situ measurements with which to verify their chemical mechanisms, leading to large discrepancies, as seen in [Marvin2017a](#) TODO: briefly talk about Marvin2017a takeaways. Christian, Brune, and Mao, [2017](#) used GEOS-Chem v9-02, with  $4^\circ \times 5^\circ$  resolution, and while the low resolution adds errors in OH concentrations and O<sub>3</sub> production rates, the errors from chemistry, meteorology, and emissions are much larger.

### Chemistry mechanisms

There is still much work to be done in models to correctly simulate the various precursors to HCHO. Often HCHO is used as a way of checking if these precursors are correctly modelled since HCHO measurements are more readily available (for instance from satellites). GEOS-Chem has recently been analysed for sensitivity for ozone along with oxidants (OH and HO<sub>2</sub>) (Christian, Brune, and Mao, [2017](#)). Christian, Brune, and Mao, [2017](#) found that GEOS-Chem ozone was most sensitive to NO<sub>2</sub> photolysis, the NO<sub>2</sub> + OH reaction rate, and various emissions.

Marvin et al., [2017](#) suggest that isoprene mechanisms in several contemporary models (including GEOS-Chem) are inadequate. They show that for a specific measurement campaign, the HCHO concentrations are underestimated in a way that can not be easily fixed through rate constant changes. Recently Marvin et al., [2017](#) compared five global ACMs isoprene mechanisms by evaluating simulated HCHO mixing ratios compared to in situ measurements from the Southeast Nexus (SENEX) aircraft campaign (in southeastern USA). They compared five models (GEOS-Chem, CB05, CB6r2, MCMv3.2, and MCMv3.3.1) and found all of them underestimated the HCHO concentrations (by 15 – 30%).

Another important factor in determining the yield of HCHO and other products from BVOCs is the local concentration of NO<sub>x</sub>. Travis et al., [2016](#) show how modelled surface ozone is overestimated due to high estimates of NO<sub>x</sub> emissions, which affect oxidative capacity and VOC reactions.

### Clouds

One of the major uncertainties in chemical, climate, radiation, and weather models is cloud formation and dynamics. Clouds are remarkably complex at a much finer scale than can be accurately modelled by global chemistry models (with current processing power). Globally over half (50-60%) of the world is covered by clouds, with ~ 10% of them being rain-clouds (Kanakidou et al., [2005](#)). Wet scavenging performed in clouds not only depends on large scale cloud processes, but also on the microphysics of aerosols being scavenged, differing between aerosol sizes and hygroscopic properties.

### Soil Moisture

Australia has a unique climate, along with soil moisture, clay content and other important properties which affect VOC emissions. These properties are poorly understood in Australia due to the continents size and the relative sparsity of population centres, which make many areas very difficult or expensive to reach. Rowntree and Bolton,

1983 show how quickly soil moisture anomalies affect rainfall and other weather systems, while Chen and Dudhia, 2001 specifically show how important fine scale soil moisture information is when modelling land surface heat flux, and energy balances. Modelled emissions are sensitive to soil moisture, especially near the soil moisture threshold (or wilting point), below which trees stop emitting isoprene and other VOCs completely as they can no longer draw water (Bauwens et al., 2016). MEGAN accounts for soil moisture by applying it as an emission factor (EF) which scales the emission rate of various species.

Droughts affects can be difficult to measure, as it is a multi-scale problem which affects various aspects of the land-air interface including plant emissions and dry deposition (Wang et al., 2017). The Standardised Precipitation Evapotranspiration Index (SPEI) is a measure of drought using TODO *SPEI Drought Index*. This product covers 1901 - 2011, and uses the average over that period as the background, in order to compare drought stressed regions against those with sufficient or excess water *SPEI Drought Index*.

## 1.6 Australia and the southern hemisphere

In Australia most long term air quality or composition measurements are performed in or near large cities. Australia is dominated by areas with little anthropogenic influence and no ground based measurements of the natural emissions taking place (VanDerA et al., 2008). Due to the lack of in-situ ground based measurements, estimates of VOC emissions are uncertain, with large scale extrapolation required Millet et al., 2006. Since many Australian cities are on the edge of regions with rich VOC emissions, it is very important to clarify the quantity, type, and cause of VOC emissions. Understanding of emissions from these areas is necessary to inform national policy on air pollution levels.

Fire emissions include a range of chemicals and each year the affects of fire or burning seasons blanket the northern and southern hemispheres independently. Biomass burning in southern Africa and South America has previously been shown to have a major influence on atmospheric composition in Australia (Oltmans et al., 2001; Gloude-mans et al., 2007; Edwards et al., 2006), particularly from July to December (Pak et al., 2003; Liu et al., 2016a).

Guenther et al., 2006 estimated that the Australian outback is among the worlds strongest isoprene emitters with forests in SE Australia having emission factors greater than  $16 \text{ mg m}^{-2} \text{ h}^{-1}$  (see figure 1.9). Measurement campaigns in SE Australia have since cast doubt on the emission factors used by MEGAN, as the Eucalyptus trees and soil moisture were poorly studied Emmerson et al., 2016. These emissions factor estimates are not well verified and measurements of isoprene (or other BVOC) emissions barely cover Australia either spatially or temporally. However, comprehensive coverage of one high yield product (HCHO) in the atmosphere over Australia exists in the form of satellite measurements.



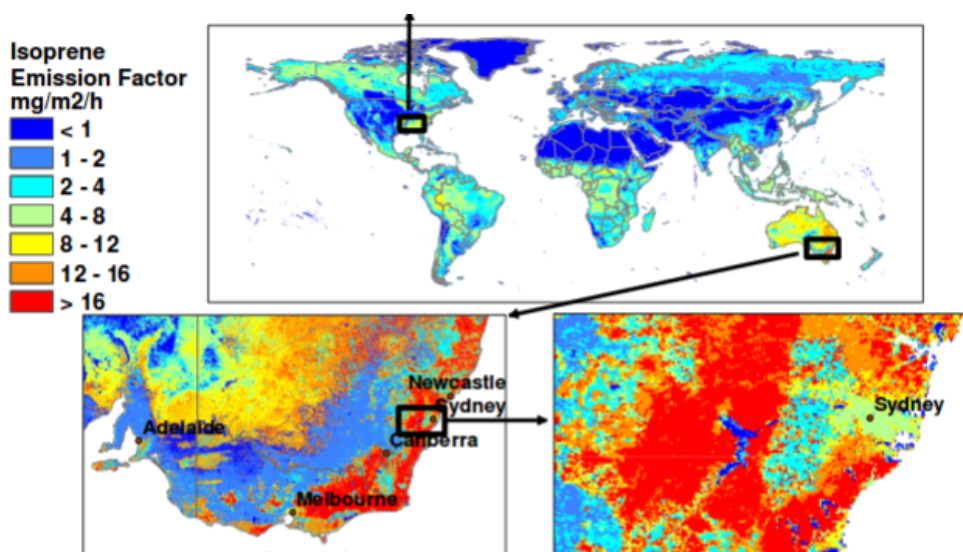


Fig. 2. Global distribution of landscape-average isoprene emission factors (mg isoprene m<sup>-2</sup> h<sup>-1</sup>). Spatial variability at the base resolution (~1 km) is shown by regional images of the southeastern U.S. and southeastern Australia.

FIGURE 1.9: Part of a figure from Guenther et al., 2006 showing global isoprene emission factors.

### 1.6.1 Ozone

Ozone levels over Australia are generally low, however it remains unclear how much we would expect this to change in the future as relatively little is known about precursors and influx for the continent. Australian air quality is monitored independently within each state, using various metrics. These metrics are measured by varying numbers of monitoring stations in each state. In New South Wales (NSW) the metrics used to determine air quality are: particulate matter (PM), O<sub>3</sub>, CO, NO<sub>2</sub>, SO<sub>2</sub>, and visibility. An air quality index equal to the worst of these metrics is used for NSW as shown at <http://www.environment.nsw.gov.au/aqms/aqitable.htm>. Similar methods are used in other states to get an idea of air quality. Measurement stations are generally located in population centres, and don't regularly measure precursor emissions. This is an important omission as naturally emitted precursor gases often get transported into cities where they affect air quality through production of O<sub>3</sub> and other pollutants.

Generally STT over Australia affects the upper troposphere only, however ozone enhancements can reach quite low during heavy storms and cyclonic weather patterns (Alexander et al., 2013)

### 1.6.2 VOCs

Bottom up inventories of VOCs remain largely uncertain due to extensive extrapolation over plant functional types, changing land cover, and parameterised environmental stressors (Guenther et al., 2000; Kanakidou et al., 2005; Millet et al., 2006). VOC emission estimates are highly sensitive to many factors, several of which are not well characterised in Australia (Sindelarova et al., 2014; Bauwens et al., 2016). Changes in parameterisation of soil moisture in the Model of Emissions of Gases and Aerosols

from Nature (MEGAN, Guenther et al., 1995) lead to massive changes in Australian isoprene emission estimates (Sindelarova et al., 2014). Over Australia MEGAN has problems involving unpublished plant functional types and their emissions, as well as poorly optimised soil moisture parameterisation (Emmerson et al., 2016).

Australia has the potential to be a major hotspot of isoprene emissions according to Guenther et al., 2006; Guenther et al., 2012, which shows heavy emissions factors in the region. Although recent work suggests that some Australian eucalypts may not be as egregious isoprene emitters as once thought Emmerson et al., 2016. Emissions in MEGAN are based on plant functional types, which can vary heavily even within species. TODO: more on Muller2008 Australia also lacks a clear estimate of emitted monoterpenes.

Emmerson et al., 2016 analyse EF sensitivity of a high resolution model of atmospheric chemistry over southeast Australia, comparing isoprene and monoterpene emissions against 4 separate campaigns. They show that the effect on total emissions is roughly linear and that no blanket EF changes are appropriate for all regions/seasons. They also mention that Australian eucalypt emissions are based on samples from young trees, which may emit more isoprene than older trees. Emmerson et al., 2016 suggest that monoterpenes may be emitted in similar quantities to isoprene, with more measurements required to determine if this is so. They compare emissions estimates from MEGAN against data from several field campaigns and see overestimated isoprene emissions, as well as underestimated monoterpene emissions. Their work suggests that MEGAN estimates of isoprene emissions may be 2-6 times too high, and monoterpene emissions  $\sim 3$  times too low over southeast Australia.

This problem is even more pronounced in Australia due to poor characterisation, or because emission factors are based on northern hemispheric data. Many plant emissions rates have not been published, such as those for any Australian acacias. Additionally soil moisture is not well quantified which has a large effect on emissions. Müller et al., 2008 show how isoprene is poorly captured by the MEGAN model and analyse the affect of changing the soil moisture parameter, which can reduce the overall bias for Australia. Sindelarova et al., 2014 show reductions in modelled Australian isoprene emissions of 50% when incorporating soil moisture in MEGAN estimates. Uncertainties in isoprene emissions could explain why models of HCHO over Australia are poor at reproducing satellite measurements (Stavrakou et al., 2009).

### 1.6.3 Measurements

TODO: Brief overview of all the measurement campaigns, pointing to Modelling and Data chapter for more details. There are relatively few measurements of isoprene in the southern hemisphere, including MUMBA(TODO CITE), other campaigns?, and very recently that girl from Macquarie University with an instrument in the daintree rainforest(TODO CITE, DESCRIBE?). For details on the MUMBA campaign see Section ???. An aircraft campaign (HIPPO) measuring isoprene was also performed in 2009-2011? TODO: ask Jenny re this one.

A particulate and air quality measurement campaign took place in Sydney using PTR-MS and GC-FID, for details see Section ??.

One method of measuring ozone in the troposphere and stratosphere is by releasing weather balloons (with attached ozone detectors) which take readings as they rise



up to around 30 km, giving a vertical profile of concentrations. Since 1986, Lauder, New Zealand (45°S, 170°E) has released ozonesondes allowing a multi-decadal analysis of ozone concentrations over the city (Brinksma et al., 2002). Kerguelan Island (49.2°S, 70.1°E), also has a record of ozonesonde profiles, which are directly in the path of biomass burning smoke plumes transported off shore from Africa (Baray et al., 2012). SHADOZ is the southern hemispheric additional ozone project, which have released sondes from 15 sites at different times <http://tropo.gsfc.nasa.gov/shadoz/>.

## 1.7 Aims

TODO: outline of aims here (FIND THESE THEY ARE SOMEWHERE)

**One of the aims in this thesis is to use the available satellite measurements to improve the estimates of isoprene emissions in Australia.** Satellites which overpass daily record reflected solar (and emitted terrestrial) radiation, and give us measurements over all of Australia. Combining satellite data with model outcomes provides a platform for the understanding of natural processes which is especially useful over Australia. Due to the low availability of in-situ data over most of the Australian continent, a combination of the models with satellite can fill the gap of understanding of emissions from Australian landscapes. Improved emissions estimates will in turn improve the accuracy of CTMs, providing better predictions of atmospheric composition and its response to ongoing environmental change.

Calculation of isoprene to HCHO yields over Australia is required to create top-down estimates. This requires among other things an idea of which VOCs are present and their yields of HCHO. The technique of determining isoprene emissions from satellite detected HCHO is called satellite inversion. **Another aim to this end is to run and become familiar with GEOS-Chem in order to determine Australian emissions and yields, and the importance of the relevant parameters.** Soil moisture plays an important role in VOC emissions, as trees under stress may stop emitting various chemicals. This is especially true for Australia due to frequent droughts and wildfires. The argument for improved understanding of land surface properties, specifically soil moisture, is an old one (Mintz, 1982; Rowntree and Bolton, 1983; Chen and Dudhia, 2001).

**To improve understanding of ozone over the southern hemisphere including Australia.** Meteorology and precursor emissions are the largest drivers of tropospheric ozone concentrations, and an improved understanding of their effects in Australia would be facilitated by an analysis of STT as well as more confidence in the emitted precursors.



# Bibliography

- Brasseur, Guy P and Daniel J Jacob (2017). *Modeling of Atmospheric Chemistry*. Cambridge University Press. DOI: [10.1017/9781316544754](https://doi.org/10.1017/9781316544754).
- Atkinson, Roger (2000). "Atmospheric chemistry of VOCs and NO(x)". In: *Atmospheric Environment* 34.12-14, pp. 2063–2101. ISSN: 13522310. DOI: [10.1016/S1352-2310\(99\)00460-4](https://doi.org/10.1016/S1352-2310(99)00460-4).
- Fuentes, J. D. et al. (2000). "Biogenic Hydrocarbons in the Atmospheric Boundary Layer: A Review". In: *Bulletin of the American Meteorological Society* 81.7, pp. 1537–1575. ISSN: 00030007. DOI: [10.1175/1520-0477\(2000\)081<1537:BHITAB>2.3.CO;2](https://doi.org/10.1175/1520-0477(2000)081<1537:BHITAB>2.3.CO;2). arXiv: [arXiv:1011.1669v3](https://arxiv.org/abs/1011.1669v3). URL: [http://journals.ametsoc.org/doi/abs/10.1175/1520-0477\(2000\)081%3C1537%3ABHITAB%3E2.3.CO%3B2](http://journals.ametsoc.org/doi/abs/10.1175/1520-0477(2000)081%3C1537%3ABHITAB%3E2.3.CO%3B2).
- Paulot, Fabien et al. (2009b). "Unexpected Epoxide Formation in the". In: *Science* 325.2009, pp. 730–733. ISSN: 0036-8075. DOI: [10.1126/science.1172910](https://doi.org/10.1126/science.1172910).
- Atkinson, Roger and Janet Arey (2003). "Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review". In: *Atmospheric Environment* 37.SUPPL. 2. ISSN: 13522310. DOI: [10.1016/S1352-2310\(03\)00391-1](https://doi.org/10.1016/S1352-2310(03)00391-1).
- Hsieh, Nan-Hung and Chung-Min Liao (2013). "Fluctuations in air pollution give risk warning signals of asthma hospitalization". In: *Atmospheric Environment* 75, pp. 206–216. DOI: [10.1016/j.atmosenv.2013.04.043](https://doi.org/10.1016/j.atmosenv.2013.04.043). URL: <http://dx.doi.org/10.1016/j.atmosenv.2013.04.043>.
- Avnery, Shiri et al. (2013). "Global crop yield reductions due to surface ozone exposure: 2. Year 2030 potential crop production losses and economic damage under two scenarios of O<sub>3</sub> pollution". In: *Atmospheric Environment* 71.13, pp. 408–409. ISSN: 13522310. DOI: [10.1016/j.atmosenv.2012.12.045](https://doi.org/10.1016/j.atmosenv.2012.12.045). URL: <http://dx.doi.org/10.1016/j.atmosenv.2011.01.002>.
- Yue, Xu et al. (2017). "Ozone and haze pollution weakens net primary productivity in China". In: *Atmospheric Chemistry and Physics* 17.9, pp. 6073–6089. ISSN: 1680-7324. DOI: [10.5194/acp-17-6073-2017](https://doi.org/10.5194/acp-17-6073-2017). URL: <https://www.atmos-chem-phys.net/17/6073/2017/>.
- Myhre, G and D Shindell (2013). *Chapter 8: Anthropogenic and Natural Radiative Forcing, in Climate Change 2013: The Physical Science Basis, Working Group 1 Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, 2013*. Fifth Assessment Report of the Intergovernmental Panel on Climate Change, 2013.
- Monks, P. S. et al. (2015). "Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer". In: *Atmospheric Chemistry and Physics* 15.15, pp. 8889–8973. ISSN: 1680-7324. DOI: [10.5194/acp-15-8889-2015](https://doi.org/10.5194/acp-15-8889-2015). URL: <http://www.atmos-chem-phys.net/15/8889/2015/>.
- Lelieveld, J. et al. (2013). "Model calculated global, regional and megacity premature mortality due to air pollution". In: *Atmospheric Chemistry and Physics* 13.14, pp. 7023–7037. ISSN: 16807324. DOI: [10.5194/acp-13-7023-2013](https://doi.org/10.5194/acp-13-7023-2013).

- Ayers, James D and William R Simpson (2006). "Measurements of N<sub>2</sub>O<sub>5</sub> near Fairbanks, Alaska". In: *Journal of Geophysical Research: Atmospheres* 111.D14, n/a–n/a. ISSN: 2156-2202. DOI: [10.1029/2006JD007070](https://doi.org/10.1029/2006JD007070). URL: <http://dx.doi.org/10.1029/2006JD007070>.
- Lelieveld, J. et al. (2009). "Severe ozone air pollution in the Persian Gulf region". In: *Atmospheric Chemistry and Physics* 9, pp. 1393–1406. ISSN: 1680-7324. DOI: [10.5194/acp-9-1393-2009](https://doi.org/10.5194/acp-9-1393-2009).
- Ashmore, M R, Lisa. Emberson, and Murray Frank (2003). *Air pollution impacts on crops and forests : a global assessment*. Ed. by Lisa Emberson, Mike Ashmore, and Frank Murray. Imperial College Press London ; River Edge, NJ, xiii, 372 p. : ISBN: 186094292.
- Stevenson, D. S. et al. (2013). "Tropospheric ozone changes, radiative forcing and attribution to emissions in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP)". In: *Atmospheric Chemistry and Physics* 13.6, pp. 3063–3085. ISSN: 16807316. DOI: [10.5194/acp-13-3063-2013](https://doi.org/10.5194/acp-13-3063-2013).
- Selin, N E et al. (2009). "Global health and economic impacts of future ozone pollution". In: *Environmental Research Letters* 4.4, p. 044014. ISSN: 1748-9326. DOI: [10.1088/1748-9326/4/4/044014](https://doi.org/10.1088/1748-9326/4/4/044014).
- Huang, Guanyu et al. (2017). "Validation of 10-year SAO OMI Ozone Profile (PROFOZ) Product Using Aura MLS Measurements". In: *Atmospheric Measurement Techniques Discussions*, pp. 1–25. ISSN: 1867-8610. DOI: [10.5194/amt-2017-92](https://doi.org/10.5194/amt-2017-92). URL: <https://www.atmos-meas-tech-discuss.net/amt-2017-92/>.
- Young, P J et al. (2017). "Tropospheric Ozone Assessment Report (TOAR): Assessment of global-scale model performance for global and regional ozone distributions, variability, and trends". In: *Elementa: Science of the Anthropocene*, pp. 0–84. ISSN: 2325-1026. DOI: [10.1525/elementa.265](https://doi.org/10.1525/elementa.265). URL: [http://eprints.lancs.ac.uk/88836/1/TOAR\\_Model\\_Performance\\_07062017.pdf](http://eprints.lancs.ac.uk/88836/1/TOAR_Model_Performance_07062017.pdf)[http://www.igacproject.org/sites/default/files/2017-05/TOAR-Model\\_Performance\\_draft\\_for\\_open\\_comment.pdf](http://www.igacproject.org/sites/default/files/2017-05/TOAR-Model_Performance_draft_for_open_comment.pdf).
- Stohl, Andreas et al. (2003). "A new perspective of stratosphere-troposphere exchange". In: *Bulletin of the American Meteorological Society* 84.11, pp. 1565–1573+1473. ISSN: 00030007. DOI: [10.1175/BAMS-84-11-1565](https://doi.org/10.1175/BAMS-84-11-1565).
- Kuang, Shi et al. (2017). "Summertime tropospheric ozone enhancement associated with a cold front passage due to stratosphere-to-troposphere transport and biomass burning: Simultaneous ground-based lidar and airborne measurements". In: *Journal of Geophysical Research: Atmospheres* 122.2, pp. 1293–1311. ISSN: 21698996. DOI: [10.1002/2016JD026078](https://doi.org/10.1002/2016JD026078). URL: <http://doi.wiley.com/10.1002/2016JD026078>.
- Sprenger, Michael, Mischa Croci Maspoli, and Heini Wernli (2003). "Tropopause folds and cross-tropopause exchange: A global investigation based upon ECMWF analyses for the time period March 2000 to February 2001". In: *Journal of Geophysical Research* 108.D12. ISSN: 2156-2202. DOI: [10.1029/2002JD002587](https://doi.org/10.1029/2002JD002587). URL: <http://dx.doi.org/10.1029/2002JD002587>.
- Ojha, Narendra et al. (2016). "Secondary ozone peaks in the troposphere over the Himalayas". In: *Atmospheric Chemistry and Physics Discussions* 17.November, pp. 1–25. ISSN: 1680-7375. DOI: [10.5194/acp-2016-908](https://doi.org/10.5194/acp-2016-908). URL: <http://www.atmos-chem-phys-discuss.net/acp-2016-908/>.

- Hegglin, Michaela I and Theodore G Shepherd (2009). "Large climate-induced changes in ultraviolet index and stratosphere-to-troposphere ozone flux". In: *Nature Geoscience* 2.10, pp. 687–691. DOI: 10.1038/ngeo604. URL: <http://dx.doi.org/10.1038/ngeo604>.
- Liu, Junhua et al. (2017). "Causes of interannual variability over the southern hemispheric tropospheric ozone maximum". In: *Atmos. Chem. Phys* 17.5, pp. 3279–3299. ISSN: 1680-7324. DOI: 10.5194/acp-17-3279-2017. URL: [www.atmos-chem-phys.net/17/3279/2017/http://www.atmos-chem-phys.net/17/3279/2017/](http://www.atmos-chem-phys.net/17/3279/2017/http://www.atmos-chem-phys.net/17/3279/2017/).
- Lin, Meiyun et al. (2015). "Climate variability modulates western US ozone air quality in spring via deep stratospheric intrusions." In: *Nature communications* 6.May, p. 7105. ISSN: 2041-1723. DOI: 10.1038/ncomms8105. URL: <http://www.nature.com/ncomms/2015/150512/ncomms8105/full/ncomms8105.html>.
- Young, P. J. et al. (2013). "Preindustrial to present-day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP)". In: *Atmospheric Chemistry and Physics* 13.10, pp. 5277–5298. ISSN: 16807316. DOI: 10.5194/acp-13-5277-2013.
- Marvin, Margaret R. et al. (2017). "Impact of evolving isoprene mechanisms on simulated formaldehyde: An inter-comparison supported by in situ observations from SENEX". In: *Atmospheric Environment* 164, pp. 325–336. ISSN: 13522310. DOI: 10.1016/j.atmosenv.2017.05.049. URL: [https://ac.els-cdn.com/S1352231017303618/1-s2.0-S1352231017303618-main.pdf?\\_tid=3de7eaaa-06ff-11e8-99a9-00000aacb360&acdnat=1517455576\\_09d7334af609ed43470155c1c42fad5fhttp://www.sciencedirect.com/science/article/pii/S1352231017303618](https://ac.els-cdn.com/S1352231017303618/1-s2.0-S1352231017303618-main.pdf?_tid=3de7eaaa-06ff-11e8-99a9-00000aacb360&acdnat=1517455576_09d7334af609ed43470155c1c42fad5fhttp://www.sciencedirect.com/science/article/pii/S1352231017303618).
- Mazzuca, Gina M. et al. (2016). "Ozone production and its sensitivity to NO<sub>x</sub> and VOCs: Results from the DISCOVER-AQ field experiment, Houston 2013". In: *Atmospheric Chemistry and Physics* 16.22, pp. 14463–14474. ISSN: 16807324. DOI: 10.5194/acp-16-14463-2016.
- Stevenson, D S et al. (2006). "Multimodel ensemble simulations of present-day and near-future tropospheric ozone". In: *Journal of Geophysical Research* 111.D8. DOI: 10.1029/2005jd006338. URL: <http://dx.doi.org/10.1029/2005JD006338>.
- Guenther, Alex et al. (2000). "Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America". In: *Atmospheric Environment* 34.12-14, pp. 2205–2230. ISSN: 13522310. DOI: 10.1016/S1352-2310(99)00465-3.
- Guenther, Alex et al. (1995). "A global model of natural volatile organic compound emissions". In: *Journal of Geophysical Research* 100.D5, pp. 8873–8892. ISSN: 0148-0227. DOI: 10.1029/94JD02950. URL: [http://onlinelibrary.wiley.com/doi/10.1029/94JD02950http://onlinelibrary.wiley.com/doi/10.1029/94JD02950/full](http://onlinelibrary.wiley.com/doi/10.1029/94JD02950/full%5Cnhttp://doi.wiley.com/10.1029/94JD02950http://onlinelibrary.wiley.com/doi/10.1029/94JD02950/full).
- Glasius, Marianne and Allen H. Goldstein (2016). "Recent Discoveries and Future Challenges in Atmospheric Organic Chemistry". In: *Environmental Science and Technology* 50.6, pp. 2754–2764. ISSN: 15205851. DOI: 10.1021/acs.est.5b05105.
- Yue, X., N. Unger, and Y. Zheng (2015). "Distinguishing the drivers of trends in land carbon fluxes and plant volatile emissions over the past 3 decades". In: *Atmospheric Chemistry and Physics* 15.20, pp. 11931–11948. ISSN: 16807324. DOI: 10.5194/acp-15-11931-2015.

- Stavrakou, T. et al. (2014). "Isoprene emissions over Asia 1979-2012: Impact of climate and land-use changes". In: *Atmospheric Chemistry and Physics* 14.9. ISSN: 16807324. DOI: [10.5194/acp-14-4587-2014](https://doi.org/10.5194/acp-14-4587-2014).
- Kwon, Hyeong-Ahn et al. (2017). "Sensitivity of formaldehyde (HCHO) column measurements from a geostationary satellite to temporal variation of the air mass factor in East Asia". In: *Atmospheric Chemistry and Physics* 17.7, pp. 4673–4686. ISSN: 1680-7324. DOI: [10.5194/acp-17-4673-2017](https://doi.org/10.5194/acp-17-4673-2017). URL: <http://www.atmos-chem-phys.net/17/4673/2017/>.
- Kanakidou, M et al. (2005). "Physics Organic aerosol and global climate modelling : a review". In: *Atmospheric Chemistry and Physics* 5, pp. 1053–1123.
- Aksoyoglu, Sebnem et al. (2017). "Secondary inorganic aerosols in Europe: sources and the significant influence of biogenic VOC emissions, especially on ammonium nitrate". In: *Atmospheric Chemistry and Physics* 17.12, pp. 7757–7773. ISSN: 1680-7324. DOI: [10.5194/acp-17-7757-2017](https://doi.org/10.5194/acp-17-7757-2017). URL: <https://www.atmos-chem-phys.net/17/7757/2017/>.
- Forster, P. et al. (2007). *Changes in Atmospheric Constituents and in Radiative Forcing*. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*[Solomon, S., D. Qin, M. Man. URL: [https://www.ipcc.ch/publications\\_and\\_data/ar4/wg1/en/ch2.html](https://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2.html) (visited on 01/14/2016).
- Lelieveld, J et al. (2015). "The contribution of outdoor air pollution sources to premature mortality on a global scale". In: *Nature* 525.7569, pp. 367–371. DOI: [10.1038/nature15371](https://doi.org/10.1038/nature15371). URL: <http://dx.doi.org/10.1038/nature15371>.
- Guenther, A et al. (2006). "Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature)". In: *Atmospheric Chemistry and Physics* 6.11, pp. 3181–3210. DOI: [10.5194/acp-6-3181-2006](https://doi.org/10.5194/acp-6-3181-2006). URL: <http://dx.doi.org/10.5194/acp-6-3181-2006>.
- Millet, Dylan B et al. (2006). "Formaldehyde distribution over North America: Implications for satellite retrievals of formaldehyde columns and isoprene emission". In: *J. Geophys. Res.* 111.D24. DOI: [10.1029/2005jd006853](https://doi.org/10.1029/2005jd006853). URL: [TODO](https://doi.org/10.1029/2005jd006853).
- Brown, S. S. et al. (2009). "Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol". In: *Atmospheric Chemistry and Physics* 9.9, pp. 3027–3042. ISSN: 16807316. DOI: [10.5194/acp-9-3027-2009](https://doi.org/10.5194/acp-9-3027-2009).
- Hoek, Gerard et al. (2013). "Long-term air pollution exposure and cardio- respiratory mortality: a review". In: *Environmental Health* 12.1, p. 43. DOI: [10.1186/1476-069x-12-43](https://doi.org/10.1186/1476-069x-12-43). URL: <http://dx.doi.org/10.1186/1476-069x-12-43>.
- Krewski, D et al. (2009). "Extended follow-up and spatial analysis of the American Cancer Society study linking particulate air pollution and mortality". In: *Res Rep Health Eff Inst* 140, pp. 5–36. ISSN: 1041-5505 (Print) 1041-5505 (Linking). URL: <http://www.ncbi.nlm.nih.gov/pubmed/19627030>.
- Silva, Raquel A et al. (2013). "Global premature mortality due to anthropogenic outdoor air pollution and the contribution of past climate change". In: *Environ. Res. Lett.* 8.3, p. 34005. DOI: [10.1088/1748-9326/8/3/034005](https://doi.org/10.1088/1748-9326/8/3/034005). URL: <http://dx.doi.org/10.1088/1748-9326/8/3/034005>.



- Kroll, Jesse H. and John H. Seinfeld (2008). "Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere". In: *Atmospheric Environment* 42.16, pp. 3593–3624. ISSN: 13522310. DOI: [10.1016/j.atmosenv.2008.01.003](https://doi.org/10.1016/j.atmosenv.2008.01.003). URL: <http://www.sciencedirect.com.ezproxy.uow.edu.au/science/article/pii/S1352231008000253>.
- Guenther, A. B. et al. (2012). "The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions". In: *Geoscientific Model Development* 5.6, pp. 1471–1492. ISSN: 1991959X. DOI: [10.5194/gmd-5-1471-2012](https://doi.org/10.5194/gmd-5-1471-2012).
- Messina, Palmira et al. (2016). "Global biogenic volatile organic compound emissions in the ORCHIDEE and MEGAN models and sensitivity to key parameters". In: *Atmospheric Chemistry and Physics* 16.22, pp. 14169–14202. ISSN: 16807324. DOI: [10.5194/acp-16-14169-2016](https://doi.org/10.5194/acp-16-14169-2016). URL: <http://www.atmos-chem-phys.net/16/14169/2016/acp-16-14169-2016.pdf>.
- Wagner, V (2002). "Are CH<sub>2</sub>O measurements in the marine boundary layer suitable for testing the current understanding of CH<sub>4</sub> photooxidation?: A model study". In: *Journal of Geophysical Research* 107.D3, p. 4029. ISSN: 0148-0227. DOI: [10.1029/2001JD000722](https://doi.org/10.1029/2001JD000722). URL: <http://doi.wiley.com/10.1029/2001JD000722>.
- Nguyen, T. B. et al. (2014). "Overview of the Focused Isoprene eXperiment at the California Institute of Technology (FIXCIT): Mechanistic chamber studies on the oxidation of biogenic compounds". In: *Atmospheric Chemistry and Physics* 14.24. ISSN: 16807324. DOI: [10.5194/acp-14-13531-2014](https://doi.org/10.5194/acp-14-13531-2014).
- Arneth, A et al. (2008). "Why are estimates of global terrestrial isoprene emissions so similar ( and why is this not so for monoterpenes )?" In: *Atmos. Chem. Phys* 8.x, pp. 4605–4620. ISSN: 1680-7375. DOI: [10.5194/acpd-8-7017-2008](https://doi.org/10.5194/acpd-8-7017-2008).
- Niinemets, U. et al. (2010). "The emission factor of volatile isoprenoids: Stress, acclimation, and developmental responses". In: *Biogeosciences* 7.7, pp. 2203–2223. ISSN: 17264170. DOI: [10.5194/bg-7-2203-2010](https://doi.org/10.5194/bg-7-2203-2010).
- Müller, Jean-François (1992). "Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases". In: *Journal of Geophysical Research: Atmospheres* 97.D4, pp. 3787–3804. ISSN: 2156-2202. DOI: [10.1029/91JD02757](https://doi.org/10.1029/91JD02757). URL: <http://dx.doi.org/10.1029/91JD02757>.
- Kefauver, Shawn C., Iolanda Filella, and Josep Peñuelas (2014). "Remote sensing of atmospheric biogenic volatile organic compounds (BVOCs) via satellite-based formaldehyde vertical column assessments". en. In: *International Journal of Remote Sensing*. URL: <http://www.tandfonline.com/doi/abs/10.1080/01431161.2014.968690#.VkqEubNM6lM>.
- Crounse, John D et al. (2012). "Atmospheric Fate of Methacrolein. 1. Peroxy Radical Isomerization Following Addition of OH and O<sub>2</sub>". In: *Physical Chemistry m*.
- Wolfe, G. M. et al. (2016). "Formaldehyde production from isoprene oxidation across NO<sub>x</sub> regimes". In: *Atmospheric Chemistry and Physics* 16.x, pp. 2597–2610. ISSN: 16807324. DOI: [10.5194/acp-16-2597-2016](https://doi.org/10.5194/acp-16-2597-2016). URL: [www.atmos-chem-phys.net/16/2597/2016/](http://www.atmos-chem-phys.net/16/2597/2016/).

- Liu, Yingjun et al. (2016b). "Isoprene photochemistry over the Amazon rainforest". In: *Proceedings of the National Academy of Sciences* 113.22, pp. 6125–6130. ISSN: 0027-8424. DOI: [10.1073/pnas.1524136113](https://doi.org/10.1073/pnas.1524136113). URL: <http://www.pnas.org/content/113/22/6125.abstract>.
- PATCHEN, AMIE K. et al. (2007). "Direct Kinetics Study of the Product-Forming Channel of the Reaction of Isoprene-Derived Hydroxyperoxy Radicals with NO". In: *International journal of Chemical Kinetics* 31.5, pp. 493–499. ISSN: 13000527. DOI: [10.1002/kin.20248](https://doi.org/10.1002/kin.20248). URL: <http://onlinelibrary.wiley.com/doi/10.1002/kin.20248/full>.
- Mao, Jingqiu et al. (2013). "Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry". In: *Journal of Geophysical Research Atmospheres* 118.19, pp. 11256–11268. ISSN: 21698996. DOI: [10.1002/jgrd.50817](https://doi.org/10.1002/jgrd.50817).
- Paulot, F. et al. (2009a). "Isoprene photooxidation: new insights into the production of acids and organic nitrates". In: *Atmospheric Chemistry and Physics* 9.4, pp. 1479–1501. ISSN: 1680-7324. DOI: [10.5194/acp-9-1479-2009](https://doi.org/10.5194/acp-9-1479-2009).
- Crounse, John D. et al. (2013). "Autoxidation of organic compounds in the atmosphere". In: *Journal of Physical Chemistry Letters* 4.20, pp. 3513–3520. ISSN: 19487185. DOI: [10.1021/jz4019207](https://doi.org/10.1021/jz4019207). URL: <http://pubs.acs.org/doi/abs/10.1021/jz4019207>.
- Lin, Ying-Hsuan et al. (2013). "Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides". In: DOI: [10.1073/pnas.1221150110](https://doi.org/10.1073/pnas.1221150110). URL: <http://www.pnas.org/content/110/17/6718.full.pdf>.
- Peeters, Jozef and Jean-Francis Muller (2010). "HOx radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence and global impact". In: *Physical Chemistry Chemical Physics* 12.42, p. 14227. ISSN: 1463-9076. DOI: [10.1039/c0cp00811g](https://doi.org/10.1039/c0cp00811g). URL: <http://pubs.rsc.org/en/content/articlepdf/2010/cp/c0cp00811g>.
- Mao, J. et al. (2012). "Insights into hydroxyl measurements and atmospheric oxidation in a California forest". In: *Atmospheric Chemistry and Physics* 12.17, pp. 8009–8020. ISSN: 16807316. DOI: [10.5194/acp-12-8009-2012](https://doi.org/10.5194/acp-12-8009-2012).
- Surratt, Jason D et al. "Reactive intermediates revealed in secondary organic aerosol formation from isoprene". In: DOI: [10.1073/pnas.0911114107](https://doi.org/10.1073/pnas.0911114107). URL: <http://www.pnas.org/content/107/15/6640.full.pdf>.
- Nguyen, Tran B. et al. (2016). "Atmospheric fates of Criegee intermediates in the ozonolysis of isoprene". In: *Phys. Chem. Chem. Phys.* 18.15, pp. 10241–10254. ISSN: 1463-9076. DOI: [10.1039/C6CP00053C](https://doi.org/10.1039/C6CP00053C). URL: <http://xlink.rsc.org/?DOI=C6CP00053C>.
- Rollins, A W et al. (2009). "Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields". In: *Atmos. Chem. Phys. Atmospheric Chemistry and Physics* 9, pp. 6685–6703. URL: [www.atmos-chem-phys.net/9/6685/2009/](http://www.atmos-chem-phys.net/9/6685/2009/).
- Intergovernmental Panel on Climate Change (IPCC): *Climate Change: The Scientific Basis* (2001). Tech. rep. Cambridge University Press. URL: <http://www.ipcc.ch/ipccreports/tar/>.
- Stocker, T.F. et al. *IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on*



- Climate Change*. Tech. rep. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. DOI: [10.1017/CB09781107415324](https://doi.org/10.1017/CB09781107415324).
- Davenport, J. J. et al. (2015). "A measurement strategy for non-dispersive ultra-violet detection of formaldehyde in indoor air : spectral analysis and interferent gases". In: *Measurement Science and Technology* 015802. December 2015, p. 15802. ISSN: 0957-0233. DOI: [10.1088/0957-0233/27/1/015802](https://doi.org/10.1088/0957-0233/27/1/015802). URL: <http://dx.doi.org/10.1088/0957-0233/27/1/015802>.
- Palmer, Paul I (2003). "Mapping isoprene emissions over North America using formaldehyde column observations from space". In: *J. Geophys. Res.* 108.D6. DOI: [10.1029/2002jd002153](https://doi.org/10.1029/2002jd002153). URL: <http://dx.doi.org/10.1029/2002jd002153>.
- Shim, Changsub et al. (2005). "Constraining global isoprene emissions with Global Ozone Monitoring Experiment (GOME) formaldehyde column measurements". In: *Journal of Geophysical Research Atmospheres* 110.24, pp. 1–14. ISSN: 01480227. DOI: [10.1029/2004JD005629](https://doi.org/10.1029/2004JD005629).
- Andreae, M O (2001). "Emission of trace gases and aerosols from biomass burning". In: *Biogeochemistry* 15.4, pp. 955–966. URL: <http://onlinelibrary.wiley.com/doi/10.1029/2000GB001382/epdf>.
- Millet, Dylan B. et al. (2008). "Spatial distribution of isoprene emissions from North America derived from formaldehyde column measurements by the OMI satellite sensor". In: *Journal of Geophysical Research Atmospheres* 113.2, pp. 1–18. ISSN: 01480227. DOI: [10.1029/2007JD008950](https://doi.org/10.1029/2007JD008950).
- Zhu, Lei et al. (2014). "Anthropogenic emissions of highly reactive volatile organic compounds in eastern Texas inferred from oversampling of satellite (OMI) measurements of HCHO columns". In: *Environmental Research Letters* 9.11, p. 114004. ISSN: 1748-9326. DOI: [10.1088/1748-9326/9/11/114004](https://doi.org/10.1088/1748-9326/9/11/114004). URL: <http://stacks.iop.org/1748-9326/9/i=11/a=114004?key=crossref.3d2869ee02fd4f0792f831ac8cbec117>.
- Fu, Tzung-may et al. (2007). "Space-based formaldehyde measurements as constraints on volatile organic compound emissions in east and south Asia and implications for ozone". In: 112, pp. 1–15. DOI: [10.1029/2006JD007853](https://doi.org/10.1029/2006JD007853).
- Emmerson, Kathryn M. et al. (2016). "Current estimates of biogenic emissions from eucalypts uncertain for southeast Australia". In: *Atmospheric Chemistry and Physics* 16.11, pp. 6997–7011. ISSN: 1680-7324. DOI: [10.5194/acp-16-6997-2016](https://doi.org/10.5194/acp-16-6997-2016). URL: <http://www.atmos-chem-phys.net/16/6997/2016/>.
- CRUTZEN, PAUL J, MARK G LAWRENCE, and ULRICH PÖSCHL (1999). "On the background photochemistry of tropospheric ozone". In: *Tellus A* 51.1, pp. 123–146. ISSN: 1600-0870. DOI: [10.1034/j.1600-0870.1999.t01-1-00010.x](https://doi.org/10.1034/j.1600-0870.1999.t01-1-00010.x). URL: <http://dx.doi.org/10.1034/j.1600-0870.1999.t01-1-00010.x>.
- Levy, Hiram (1972). "Photochemistry of the lower troposphere". In: *Planetary and Space Science* 20.6, pp. 919–935. ISSN: 00320633. DOI: [10.1016/0032-0633\(72\)90177-8](https://doi.org/10.1016/0032-0633(72)90177-8).
- Franco, B. et al. (2015). "Retrievals of formaldehyde from ground-based FTIR and MAX-DOAS observations at the Jungfraujoch station and comparisons with GEOS-Chem and IMAGES model simulations". In: *Atmospheric Measurement Techniques* 8.4, pp. 1733–1756. ISSN: 18678548. DOI: [10.5194/amt-8-1733-2015](https://doi.org/10.5194/amt-8-1733-2015).
- Gonzalez Abad, G. et al. (2015). "Updated Smithsonian Astrophysical Observatory Ozone Monitoring Instrument (SAO OMI) formaldehyde retrieval". In: *Atmospheric*

- Measurement Techniques* 8.1, pp. 19–32. ISSN: 18678548. DOI: [10.5194/amt-8-19-2015](https://doi.org/10.5194/amt-8-19-2015).
- Lee, Anita et al. (2006). “Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes”. In: *Atmospheric Chemistry and Physics* 11.1, pp. 1–18. DOI: [10.1029/2005JD006437](https://doi.org/10.1029/2005JD006437).
- Hak, C. et al. (2005). “Intercomparison of four different in-situ techniques for ambient formaldehyde measurements in urban air”. In: *Atmospheric Chemistry and Physics Discussions* 5.3, pp. 2897–2945. ISSN: 1680-7316. DOI: [10.5194/acpd-5-2897-2005](https://doi.org/10.5194/acpd-5-2897-2005).
- Chevallier, F. et al. (2012). “The formaldehyde budget as seen by a global-scale multi-constraint and multi-species inversion system”. In: *Atmospheric Chemistry and Physics* 12.15, pp. 6699–6721. ISSN: 16807316. DOI: [10.5194/acp-12-6699-2012](https://doi.org/10.5194/acp-12-6699-2012). URL: <http://www.atmos-chem-phys.net/12/6699/2012/acp-12-6699-2012.pdf>.
- EUMETSAT (2015). GOME2. URL: <http://www.eumetsat.int/website/home/Satellites/CurrentSatellites/Metop/MetopDesign/GOME2/index.html>.
- Dufour, G. et al. (2008). “SCIAMACHY formaldehyde observations: constraint for isoprene emissions over Europe?” In: *Atmospheric Chemistry and Physics* 8.6, pp. 19273–19312. ISSN: 1680-7324. DOI: [10.5194/acpd-8-19273-2008](https://doi.org/10.5194/acpd-8-19273-2008).
- Marais, E A et al. (2012). “Isoprene emissions in Africa inferred from OMI observations of formaldehyde columns”. In: *Atmospheric Chemistry and Physics* 12.3, pp. 7475–7520. DOI: [10.5194/acp-12-6219-2012](https://doi.org/10.5194/acp-12-6219-2012). URL: <http://dx.doi.org/10.5194/acp-12-6219-2012>.
- Bauwens, M et al. (2013). “Satellite-based isoprene emission estimates (2007–2012) from the GlobEmission project”. In: *Proceedings of the ACCENT-Plus Symposium, Atmospheric Composition Change-Policy Support and Science, Urbino*, pp. 17–20.
- Bauwens, Maite et al. (2016). “Nine years of global hydrocarbon emissions based on source inversion of OMI formaldehyde observations”. In: *Atmospheric Chemistry and Physics Discussions* March, pp. 1–45. ISSN: 1680-7375. DOI: [10.5194/acp-2016-221](https://doi.org/10.5194/acp-2016-221). URL: <http://www.atmos-chem-phys-discuss.net/acp-2016-221/>.
- Jacob, Daniel J (1999). *Introduction to Atmospheric Chemistry*. Ed. by Daniel J Jacob. Princeton University Press. URL: <http://acmg.seas.harvard.edu/people/faculty/djj/book/index.html>.
- Zhang, Yang et al. (2012). “Impact of gas-phase mechanisms on Weather Research Forecasting Model with Chemistry (WRF/Chem) predictions: Mechanism implementation and comparative evaluation”. In: *Journal of Geophysical Research: Atmospheres* 117.D1, n/a–n/a. DOI: [10.1029/2011JD015775](https://doi.org/10.1029/2011JD015775). URL: <http://doi.wiley.com/10.1029/2011JD015775>.
- Marais, E A et al. (2014). “Improved model of isoprene emissions in Africa using Ozone Monitoring Instrument (OMI) satellite observations of formaldehyde: implications for oxidants and particulate matter”. In: *Atmospheric Chemistry and Physics* 14.15, pp. 7693–7703. DOI: [10.5194/acp-14-7693-2014](https://doi.org/10.5194/acp-14-7693-2014). URL: <http://dx.doi.org/10.5194/acp-14-7693-2014>.
- Miller, C. et al. (2014). “Glyoxal retrieval from the Ozone Monitoring Instrument”. In: *Atmospheric Measurement Techniques* 7.11, pp. 3891–3907. ISSN: 1867-8548. DOI: [10.5194/amt-7-3891-2014](https://doi.org/10.5194/amt-7-3891-2014). URL: <http://www.atmos-meas-tech.net/7/3891/2014/>.
- Zeng, G. et al. (2015). “Multi-model simulation of CO and HCHO in the Southern Hemisphere: comparison with observations and impact of biogenic emissions”. In: *Atmospheric Chemistry and Physics* 15.13, pp. 7217–7245. ISSN: 1680-7324. DOI:

- 10.5194/acp-15-7217-2015. URL: <http://www.atmos-chem-phys.net/15/7217/2015/>.
- Niinemetts, U. et al. (1999). "A model of isoprene emission based on energetic requirements for isoprene synthesis and leaf photosynthetic properties for Liquidambar and Quercus". In: *Plant, Cell and Environment* 22.11, pp. 1319–1335. ISSN: 01407791. DOI: 10.1046/j.1365-3040.1999.00505.x.
- Arneth, Almut et al. (2007). "CO<sub>2</sub> inhibition of global terrestrial isoprene emissions: Potential implications for atmospheric chemistry". In: *Geophysical Research Letters* 34.18, p. L18813. DOI: 10.1029/2007GL030615. URL: <http://doi.wiley.com/10.1029/2007GL030615>.
- Hewitt, C N et al. (2011). "Ground-level ozone influenced by circadian control of isoprene emissions". In: *Nature Geoscience* 4.10, pp. 671–674. DOI: 10.1038/ngeo1271. URL: <http://dx.doi.org/10.1038/ngeo1271>.
- Fan, Jiwen and Renyi Zhang (2004). "Atmospheric oxidation mechanism of isoprene". In: *Environmental Chemistry* 1.3, pp. 140–149. ISSN: 14482517. DOI: 10.1071/EN04045. URL: <http://dx.doi.org/10.1071/en04045>.
- Müller, J.-F. et al. (2008). "Global isoprene emissions estimated using MEGAN ECMWF analyses and a detailed canopy environment model". In: *Atmospheric Chemistry and Physics Discussions* 7.6, pp. 15373–15407. DOI: 10.5194/acpd-7-15373-2007. URL: <http://dx.doi.org/10.5194/acpd-7-15373-2007>.
- Winters, Anthony J et al. (2009). "Emissions of isoprene, monoterpene and short-chained carbonyl compounds from Eucalyptus spp. in southern Australia". In: *Atmospheric Environment* 43.19, pp. 3035–3043. ISSN: 13522310. DOI: 10.1016/j.atmosenv.2009.03.026.
- Wild, Oliver and Michael J. Prather (2006). "Global tropospheric ozone modeling: Quantifying errors due to grid resolution". In: *Journal of Geophysical Research Atmospheres* 111.11, pp. 1–14. ISSN: 01480227. DOI: 10.1029/2005JD006605.
- Christian, Kenneth E, William H Brune, and Jingqiu Mao (2017). "Global sensitivity analysis of the GEOS-Chem chemical transport model: ozone and hydrogen oxides during ARCTAS (2008)". In: *Atmos. Chem. Phys* 17, pp. 3769–3784. DOI: 10.5194/acp-17-3769-2017. URL: [www.atmos-chem-phys.net/17/3769/2017/](http://www.atmos-chem-phys.net/17/3769/2017/).
- Travis, Katherine R et al. (2016). "Why do models overestimate surface ozone in the Southeast United States?" In: *Atmos. Chem. Phys* 16, pp. 13561–13577. DOI: 10.5194/acp-16-13561-2016. URL: [www.atmos-chem-phys.net/16/13561/2016/](http://www.atmos-chem-phys.net/16/13561/2016/).
- Rowntree, P. R. and J. A. Bolton (1983). "Simulation of the atmospheric response to soil moisture anomalies over Europe". In: *Quarterly Journal of the Royal Meteorological Society* 109.461, pp. 501–526. ISSN: 00359009. DOI: 10.1002/qj.49710946105. URL: <http://doi.wiley.com/10.1002/qj.49710946105>.
- Chen, Fei and Jimmy Dudhia (2001). "Coupling an Advanced Land Surface–Hydrology Model with the Penn State–NCAR MM5 Modeling System. Part I: Model Implementation and Sensitivity". In: *Monthly Weather Review* 129. URL: <https://journals.ametsoc.org/doi/pdf/10.1175/1520-0493%282001%29129%3C0569%3ACAAALSH%3E2.0.CO%3B2>.
- Wang, Yuxuan et al. (2017). "Adverse effects of increasing drought on air quality via natural processes". In: *Atmos. Chem. Phys* 17.19, pp. 12827–12843. DOI: 10.5194/

- acp-17-12827-2017. URL: <https://www.atmos-chem-phys.net/17/12827/2017/acp-17-12827-2017.pdf>.
- SPEI Drought Index. URL: <http://spei.csic.es/home.html> (visited on 12/19/2017).
- VanDerA, R J et al. (2008). "Trends seasonal variability and dominant NO<sub>x</sub> source derived from a ten year record of NO<sub>2</sub> measured from space". In: *J. Geophys. Res.* 113.D4. DOI: [10.1029/2007jd009021](https://doi.org/10.1029/2007jd009021). URL: <http://dx.doi.org/10.1029/2007jd009021>.
- Oltmans, J et al. (2001). "Ozone in the Pacific tropical troposphere from ozonesonde observations". In: *Journal of Geophysical Research* 106.D23, pp. 32503–32525.
- Gloudemans, Annemieke et al. (2007). "Evidence for long-range transport of carbon monoxide in the Southern Hemisphere from SCIAMACHY observations". In: *European Space Agency, (Special Publication)* 33.SP-636, pp. 1–5. ISSN: 03796566. DOI: [10.1029/2006GL026804](https://doi.org/10.1029/2006GL026804).
- Edwards, D. P. et al. (2006). "Satellite-observed pollution from Southern Hemisphere biomass burning". In: *Journal of Geophysical Research* 111.14, pp. 1–17. ISSN: 01480227. DOI: [10.1029/2005JD006655](https://doi.org/10.1029/2005JD006655).
- Pak, B.C.a et al. (2003). "Measurements of biomass burning influences in the troposphere over southeast Australia during the SAFARI 2000 dry season campaign". In: *Journal of Geophysical Research* 108.13, pp. 1–10. ISSN: 0148-0227. DOI: [10.1029/2002JD002343](https://doi.org/10.1029/2002JD002343). URL: <http://www.scopus.com/inward/record.url?eid=2-s2.0-0742322536&partnerID=40&md5=cafaeef03b948fb456696583ed3ab9a5>.
- Liu, Junhua et al. (2016a). "Causes of interannual variability of tropospheric ozone over the Southern Ocean". In: *Atmospheric Chemistry and Physics Discussions* October, pp. 1–46. ISSN: 1680-7316. DOI: [10.5194/ACP-2016-692](https://doi.org/10.5194/ACP-2016-692).
- Alexander, S. P. et al. (2013). "High resolution VHF radar measurements of tropopause structure and variability at Davis, Antarctica (69 S, 78 E)". In: *Atmospheric Chemistry and Physics* 13.6, pp. 3121–3132. ISSN: 16807324. DOI: [10.5194/acp-13-3121-2013](https://doi.org/10.5194/acp-13-3121-2013). URL: <http://www.atmos-chem-phys.net/13/3121/2013/>.
- Sindelarova, K. et al. (2014). "Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years". In: *Atmospheric Chemistry and Physics* 14.17, pp. 9317–9341. ISSN: 16807324. DOI: [10.5194/acp-14-9317-2014](https://doi.org/10.5194/acp-14-9317-2014). arXiv: [arXiv:1011.1669v3](https://arxiv.org/abs/1011.1669v3).
- Stavrakou, T et al. (2009). "Evaluating the performance of pyrogenic and biogenic emission inventories against one decade of space-based formaldehyde columns". In: *Atmospheric Chemistry and Physics* 9.3, pp. 1037–1060. DOI: [10.5194/acp-9-1037-2009](https://doi.org/10.5194/acp-9-1037-2009). URL: <http://dx.doi.org/10.5194/acp-9-1037-2009>.
- Brinksmas, E. J. et al. (2002). "Five years of observations of ozone profiles over Lauder, New Zealand". In: *Journal of Geophysical Research* 107.D14, pp. 1–11. ISSN: 0148-0227. DOI: [10.1029/2001JD000737](https://doi.org/10.1029/2001JD000737). URL: <http://doi.wiley.com/10.1029/2001JD000737>.
- Baray, Jean-Luc et al. (2012). "One year ozonesonde measurements at Kerguelen Island (49.2S, 70.1E): Influence of stratosphere-to-troposphere exchange and long-range transport of biomass burning plumes". In: *Journal of Geophysical Research* 117.D6. ISSN: 2156-2202. DOI: [10.1029/2011JD016717](https://doi.org/10.1029/2011JD016717). URL: <http://dx.doi.org/10.1029/2011JD016717>.

- 
- Mintz, Y (1982). "The sensitivity of numerically simulated climates to land surface conditions". In: *Land Surface Processes in Atmospheric General Circulation Models*, pp. 109–111.